# THE DISSOCIATION PRESSURES OF HYDRATED DOUBLE SALTS.

A THESIS presented to the SENATE of the
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by

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# INTRODUCTORY.

It has long been known that a hydrated salt, present in an enclosed space, loses some of its water of hydration, until there is set up within the space a definite aqueous vapour pressure, which for any particular salt is constant at constant tempersture. This experimental fact, first enunciated by Wiedemann in 1866, received its explanation on the formulation of the Phase Rule. The pressure is an equilibrium pressure in the system: salt hydrate - lower hydrate - water vapour, and according to the rule, such a system, consisting of two components, (salt and water), present in three phases, (one gaseous and two solid), possesses only one degree of freedom, so that to every definite temperature there corresponds a fixed value of the vapour pressure.

Numerous measurements of the dissociation pressures of hydrated salt systems have been made. These, however, have chiefly been carried out on isolated examples of salts, and few attempts have been made to correlate these measurements, or to determine upon what factors the magnitude of the dissociation pressure of a hydrated salt depends.

The present research was undertaken with the object of discovering some relationship between the chemical and physical characters of a salt and the magnitude of the dissociation pressure developed when it is in contact with its next lower hydrate.

To secure as wide a field as possible for the investigation the well known series of double sulphates and selenates of the types $RSO_4$, $M_2SO_4$, $6H_2O$ and $RSeO_4$, $M_2SeO_4$, $6H_2O$, was chosen. In these formulae M represents the atom of an alkali metal (K, Rb, or Cs) or of univalent thallium or the group $NH_4$, and R the atom of a bivalent metal (Mn, Mg, Fe, Co, Ni, Cu, Zn,

or Cd). Double chromates of the same type also exist, and the investigation was extended to these as well.

It is obvious that for comparative purposes, not only must the salts chosen contain some element or group in common and be hydrated to the same degree, but also on dissociation they must yield lower hydrates with the same number of molecules of water of crystallisation. The first two conditions are, of course, fulfilled by the series chosen. The third condition was also found to hold with all the members of the double sulphate and selenate groups examined, with the exception of the salts containing magnesium and iron. The first stage in the dehydration of the two latter types of double salts results in the formation of tetrahydrates of the type $RSO_4$, $M_2SO_4$, $4H_2O$, whereas in all other cases dihydrates of the type $RSO_4$, $M_2SO_4$, $2H_2O$ were formed. The double chromate examined yielded on dehydration only the anhydrous salt.

Double sulphates of the above type were first investigated by Graham[1] (Phil. Mag. (3), 6., 1835, 420), who prepared several double sulphates and investigated the lower hydrates produced when the hexahydrated salts were heated in air. A very complete study of the crystallographic and physical properties of the same double sulphates and selenates was carried out by Tutton[2,3] in a classic research commenced in 1890 (J.C.S. 1893, 63, 337.) and concluded, after thirty-two years work, in 1922. (Proc. Roy. Soc., 1922, (A), 101, 225). The double sulphates and selenates form two of the most important series of isomorphous salts known, both groups belonging to the monoclinic system. Tutton's "main results may be summarized in the statement that the progression in the atomic sequence number, and its attendant progression in the size of the atom, is accompanied by a similarly definite progression in the

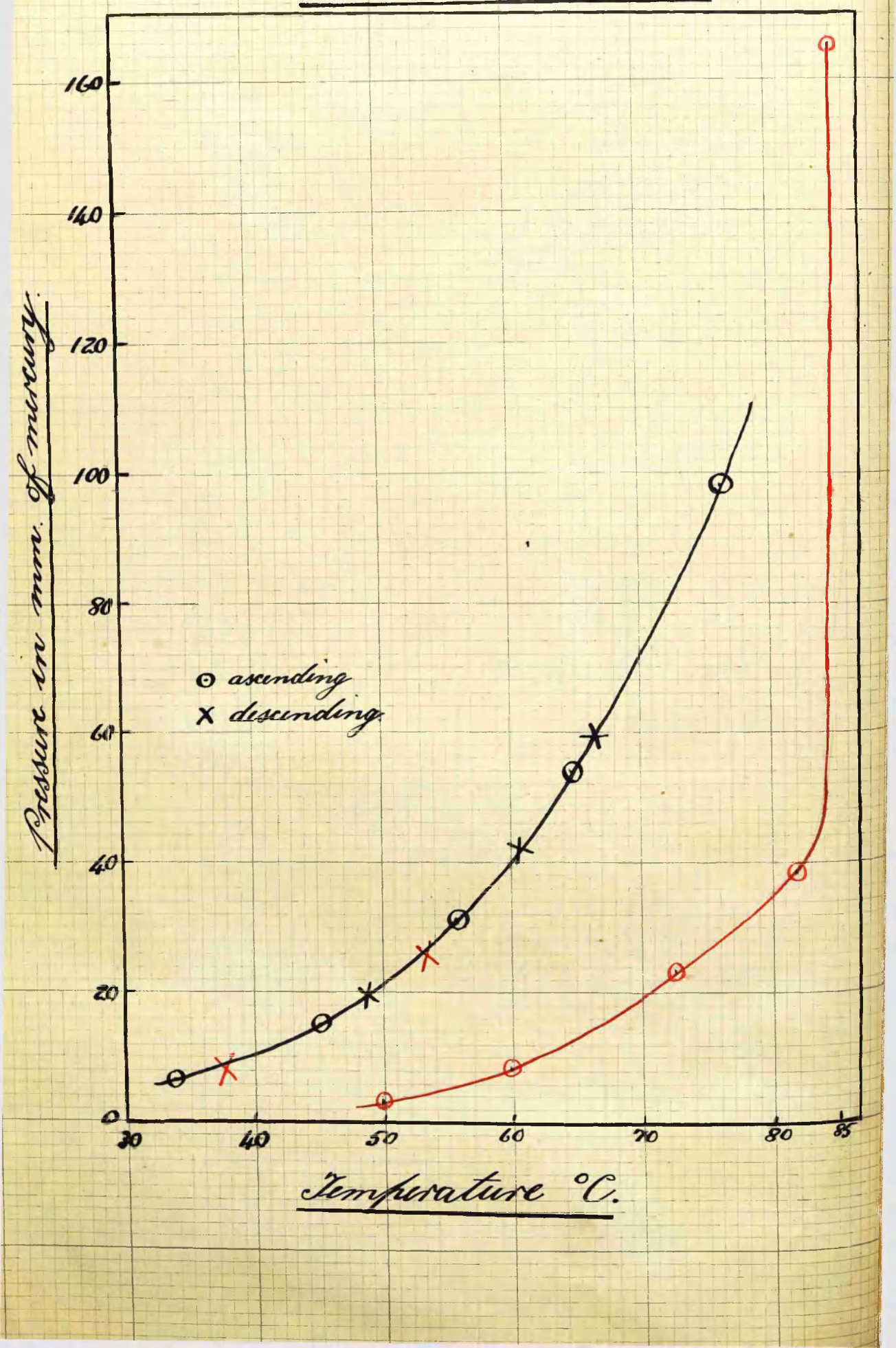
characters, external or internal, of the crystals of these isomorphous ..... monoclinic series, when the potassium in the initial salt of the series is replaced by rubidium, and the rubidium in turn replaced by Caesium ..... The ammonium salts are almost perfectly isostructural with the analogous rubidium salts, the replacement of rubidium atoms by ammonium ($NH_4$) radicals involving practically no change in the relative dimensions of the structural cell edges".*

The dissociation pressures of certain of the hexahydrated double sulphates and selenates (and also of the alums) have been studied by Ephraim and Wagner,[5] in the course of a series of researches on the strength of residual valency forces (Berichte, 1917, 50, 1089). The work of these investigators, in this case, is very much open to criticism. They seem to have taken no precautions to ensure the presence of the lower hydrate in the tensimeter, which, as will be shown later, is an absolute necessity, if the true dissociation pressure is to be observed. In consequence, their results, when expressed graphically, reveal such irregularities that it is difficult to understand how they arrived at any generalisation whatsoever.

* Friend's "Text Book of Inorganic Chemistry" Vol.II, P.229.

# Fig. I.

## Dissociation Pressure curves of Nickel Potassium Sulphate.



## INDUCTION PHENOMENA.

As just mentioned, it is of course necessary for purposes of comparison, in studying the dissociation pressures of a series of salts, that the hydrate participating in the equilibrium should be known, but, moreover, it will now be shewn that it is absolutely essential that, during the pressure measurements, both hydrates should be present in the tensimeter initially. If this is not the case equilibrium will in many cases be reached very slowly, and even a false equilibrium will be set up. Thus, in the following table, are given the pressure readings obtained when nickel potassium sulphate hexahydrate, $NiSO_4K_2SO_46H_2O$ only, was placed in the tensimeter without any trace of the lower hydrate $NiSO_4K_2SO_42H_2O$.

| Temp. °C. | Pressure. Rising | Falling. |
|---|---|---|
| 49.9 | 3.5 | - |
| 59.9 | 8.1 | - |
| 72.5 | 21.7 | - |
| 82.0 | 39.1 | - |
| 85.1 | 165.5 | - |
| 53.8 | - | 25.2 |
| 37.6 | - | 8.4 |

The first two readings were taken at intervals of three days and the others at intervals of a day. In each instance the pressure had apparently reached a constant value. In Fig. I the results are plotted graphically in red, so that they may be compared with the true dissociation curve (in black) of the system,

$$NiSO_4K_2SO_4,\ 6H_2O - NiSO_4K_2SO_42H_2O - \text{water vapour},$$

which was obtained from a mixture containing 20% of the dihydrate.

It will be observed that low values of the vapour pressure are obtained until the temperature reaches 85°C. There is

then a very sudden and a very great rise in pressure to the value obtainable when both hydrates are present in the tensimeter. On lowering the temperature, the original values of the pressure are not obtained, but values approximating to the true vapour pressure in the hexahydrate - dihydrate system. If dihydrate and hexahydrate are present initially then the pressure values obtained with both ascending and descending temperatures lie, as may be seen from the figure, on the same curve. The temperature, 85°C., at which the sudden rise occurs corresponds to the temperature at which the hexahydrate loses four molecules of water when heated in an air-oven.

If, now, the results of Ephraim and Wagner (loc. cit.) are examined (~~see Appendix~~), it will be observed that in practically every case their curves show this phenomenon. Until a certain temperature is reached, varying with each salt, the pressures are low; then there is a very sudden rise to a high value corresponding probably to the formation of the lower hydrate whose presence in the tensimeter they neglected to ensure. At high temperatures the values of the dissociation pressures obtained by these investigators approximate fairly well to those obtained in the present investigation; otherwise their results are of little or no value (as measurements of equilibrium pressures in hydrated salt systems). An examination of the curves in the appendix will show the difficulty of deducing any generalisation from their data.

The phenomena described above are intimately connected with the induction period in the dehydration of certain salts investigated by Rae,[6] (J.C.S. 109, 1229, 1916), working principally with copper sulphate pentahydrate. Rae found that when this salt was submitted to dehydrating action, either

in a desiccator over sulphuric acid, or by heating it to a constant temperature in air, in opposition to the law of mass action, water was lost at only an exceedingly slow rate at first. Once started, however, the reaction proceeded rapidly, but instead of the trihydrate being produced, as would be expected in this case, a salt containing much less water, of the composition $CuSO_4 \cdot \frac{1}{2}H_2O$, was obtained. If now this dehydrated salt was allowed to take up water again, reforming the pentahydrate, and once more exposed to the dehydrating agency, the reaction proceeded normally and the trihydrate was formed. Rae regarded this as a supersaturation effect. On dehydrating the second time it was assumed that a small quantity of the trihydrate was present from the start to form nuclei of efflorescence which determine the course of the reaction.

Very many fine examples of this induction lag have been found among the salts examined in the present investigation. Thus, for example, nickel potassium sulphate hexahydrate when first heated in an air oven does not lose water until the temperature reaches 105°C. The yellow anhydrous salt is produced. If this is now allowed to rehydrate by standing in air the original green hexahydrate is formed. On further heating the salt now loses water at as low a temperature as 80°C and the dihydrate is obtained, which is green in colour like the hexahydrate. Again, cobalt potassium sulphate when heated for the first time loses water at 95°C, forming the deep violet anhydrous salt. Rehydration of this and further heating results in a loss at a temperature as low as 80°C, yielding a dihydrate, which like the hexahydrate, is reddish-pink in colour. These two dihydrates once obtained can be heated to well over 100°C without further loss of water occurring.

The induction lag was found to be well marked in the case of the double salts formed by nickel, cobalt, zinc, and magnesium, (not, however, with magnesium potassium sulphate), but not noticeable in the case of those formed by cadmium, manganese, and copper, which exhibit much higher dissociation pressures than the first mentioned group.

The induction effect, then, is probably connected with the low pressure observed over a hydrated salt when no precautions are taken to insure the presence of the next lower hydrate. The salt loses water to form either an unstable hydrate with lower water content than that of the stable lower hydrate, or the anhydrous salt. This compound passes only very slowly into the stable lower hydrate.

Partington[7] (J.C.S., 1911, 99, 475) has pointed out that the mobile equilibrium between an isotropic liquid and its vapour is greatly different from the equilibrium in a salt hydrate system, where the molecules of water cannot return to their original positions in the first space lattice. According to his views, the violent disruption of the crystal lattice, when water is lost, produces an unstable, probably amorphous lower hydrate which slowly passes into a stable crystalline modific-:ation. The formation of an efflorescence region corresponds to a period of low vapour pressure. Once formed, however, the pressure over the system containing the amorphous hydrate is greater than the final pressure in the system containing the stable lower hydrate, into which the higher hydrate - amorphous hydrate system passes. Higher pressures, however, than those finally obtained, have not been observed in the present invest-

:igation. But, as Partington remarks, "The molecular theory of dehydration of a crystalline hydrate has, along with other dissociation phenomena in heterogeneous systems of similar character, offered difficulties which do not appear to be overcome even at present.

# EXPERIMENTAL.

## Preparation of the Double Salts.

The double sulphates were prepared by mixing hot saturated solutions of equivalent quantities of the two simple sulphates, and recrystallising the double salt obtained on cooling. Usually from 15-20 grammes of double salt was contained in the solution to be crystallised. The salts so obtained were air dried.

Rubidium sulphate was prepared from Rubidium nitrate (Merck's reagent) by heating with sulphuric acid and subsequent ignition, and was also obtained directly from Poulenc Frères. Caesium chloride and sulphate was also obtained from Poulenc Frères. Thallous sulphate was prepared by dissolving metallic thallium, a supply of which happened to be available, in sulphuric acid, evaporating to dryness, and heating gently. The product was then recrystallised. These salts were tested spectroscopically for purity, only the most minute trace of sodium being detected.

Selenium was the starting point in the preparation of the double selenates. It was oxidised by nitric acid to selenious acid. The product, after being freed from nitric acid, by repeated evaporation with water was converted into selenium dioxide and sublimed. The sublimate was then dissolved in water and oxidized by bubbling chlorine through the solution. Copper carbonate was added from time to time until all the selenium was present as copper selenate. This was then separated by evaporation of the solution, under reduced pressure below 60°C., since copper selenate solutions heated above 64°C. rapidly deposit a green basic salt. The dried product was then extracted with acetone in a Soxhlet

apparatus to free it from cupric chloride (Dennis and Koller,[8] J. Am. Chem. Soc. 1919, 41, 949), and then air dried.

On electrolysing the copper selenate in warm saturated solution with a current of 5 amp. and an E.M.F. of 3 volts, according to the method given by Metzner[9] (Compt. Rend. 1898, 127, 54) a solution of selenic acid was obtained. By neutralisation of this solution with the different metallic oxides or hydroxides the simple selenates were prepared. The double selenates were then obtained in similar fashion to the double sulphates.

The double chromate was prepared by the method described by Briggs[10] (J.C.S. 1903, 83, 392), i.e. by mixing saturated solutions of ammonium chromate and nickel acetate at a low temperature.

In each case the purity of the salt obtained was tested by carrying out an estimation of the total water content and an estimation either of the acidic radicle or of the bivalent metal present.

## Preparation of Hydrates.

Cumming[11] (J.C.S. 1910, 97, 596) has investigated the various methods used for the discovery of hydrates. Most of these, as he points out, such as solubility determinations, determinations of transition points, etc., are really only suited for the detection of hydrates, and not for their isolation, and, moreover, have other disadvantages.

A practical method for the preparation of hydrates consists of desiccation over sulphuric acid of various strengths, and hence of various aqueous vapour pressures. Cumming's method consisted in dehydrating the hydrated salt by means of the anhydrous salt, and thus obtaining the lowest hydrate pure. The lowest hydrate was then used to dehydrate a further quantity of the fully dehydrated salt and so on. In this way the whole series of hydrates formed by a salt could be prepared pure.

This method, however, is obviously too long a process for an investigation of the present type, especially with salts possessing a low dissociation pressure. Hence a much simpler method for the isolation of the lower hydrates of the double salts was adopted.

Originally a method suggested by Hannay[12] and employed by Ramsay,[13] (J.C.S. 1877. 32, 395), in his work on the hydrated oxides of iron and aluminium was used. This well known method consists in measuring the rate of dehydration of the hydrate at constant temperature by weighing a small quantity of the salt at intervals of time.

Small weighed samples (0.2 - 0.3 gm.) of the finely powdered salt were exposed on watch glasses in a water-jacketted oven maintained within 1° of constant temperature by means of a thermoregulator. The watch glasses were weighed at intervals, and on plotting the loss in weight expressed as molecules of water per molecule of original hydrated salt

against time curves were obtained which apparently became horizontal after the loss of an integral number of molecules.

This method worked fairly well with the double sulphates formed by copper. Dehydration once started, however, proceeds so rapidly that the initial portions of the curve are of little use and it is sufficient merely to maintain a weighed quantity of the salt in the oven at a definite temperature for some time and then raise the temperature by 10° steps until loss occurs, when in some cases at least an integral number of water molecules are lost.

With salts showing an induction lag, Hannay's method is obviously of little use, and as most of the salts studied show this lag, it was not used for them. In these cases the hexahydrated salt was placed in the oven and the temperature raised until loss of water occurred, the salt passing into the anhydrous condition or into a lower hydrate than that finally obtained. The dehydrated salt was then allowed to rehydrate in air at ordinary temperature, and once more heated. After this treatment the hexahydrate lost water at a lower temperature than before and formed the next lower hydrate, not the anhydrous salt. Sometimes a repetition of the preliminary dehydration was necessary before this result was obtained (See p. 6 ).

In Figs. II and III are given the dehydration curves of copper potassium sulphate and copper ammonium sulphate respectively. The data relative to the dehydration of the other salts will be found under each individual salt in the section devoted to the pressure measurements.

In Table I are given the data from which the curves in Fig. II were constructed.

# Fig II.

## Dehydration curves of Copper Potassium Sulphate at 45°C., 39°C., and 32°C.

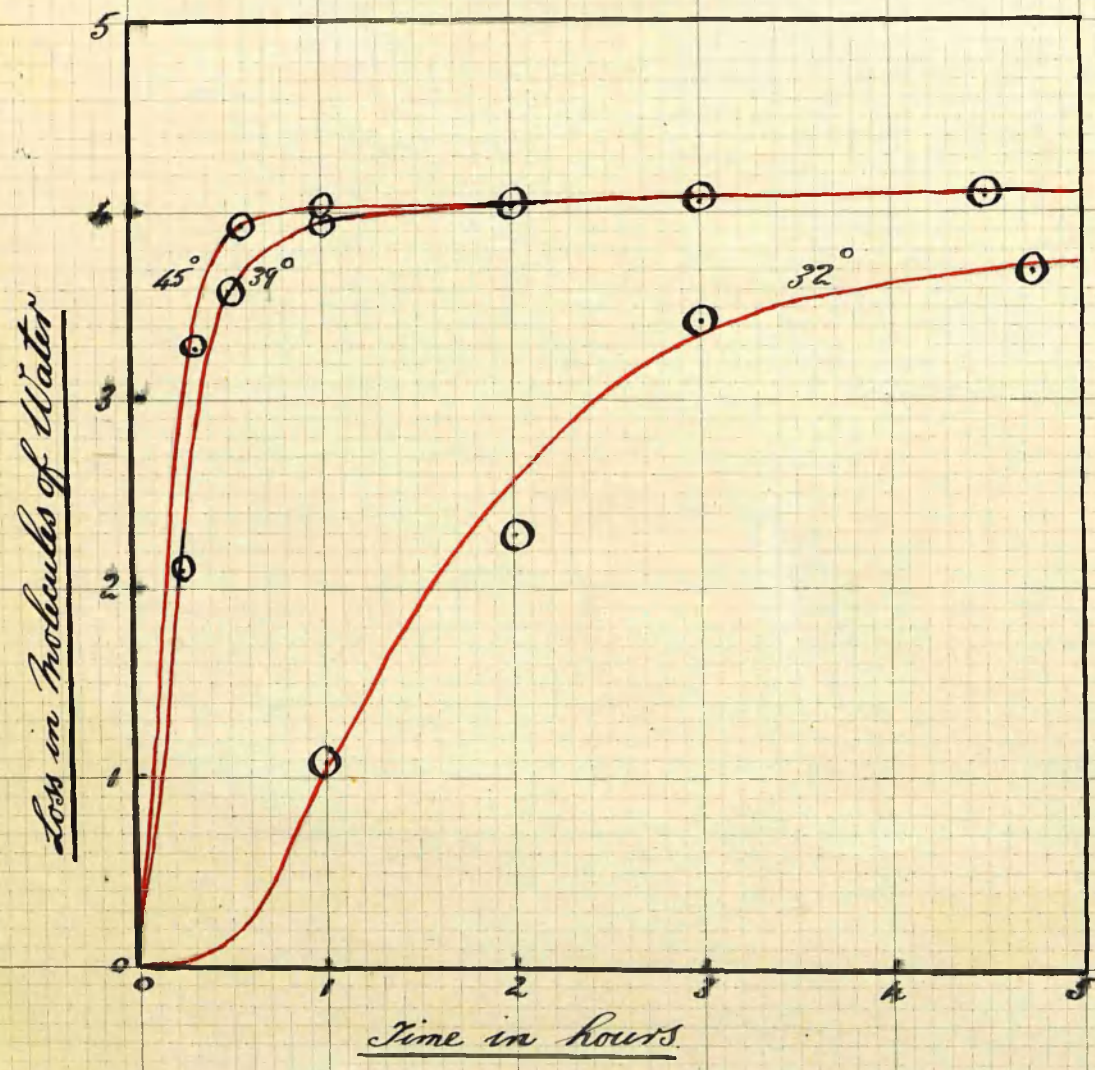


TABLE I.

Copper Potassium Sulphate.

| Temp. °C. | Weight of salt taken. gm. | Loss in Wt. gm. | Loss in mols. of water. | Time. hrs. |
|---|---|---|---|---|
| 45 | .2028 | .0270 | 3.27 | 0.33 |
| " | .2028 | .0324 | 3.92 | 0.58 |
| " | .2015 | .0330 | 4.02 | 1.00 |
| " | .2005 | .0328 | 4.02 | 2.00 |
| " | .2012 | .0332 | 4.05 | 3.00 |
| " | .2041 | .0340 | 4.09 | 4.50 |
| 39 | .2012 | .0172 | 2.10 | 0.25 |
| " | .2012 | .0294 | 3.59 | 0.50 |
| " | .2028 | .0327 | 3.96 | 1.00 |
| " | .2012 | .0330 | 4.03 | 2.00 |
| 32 | .2023 | .0090 | 1.09 | 1.00 |
| " | .2028 | .0189 | 2.29 | 2.00 |
| " | .2012 | .0279 | 3.41 | 3.00 |
| " | .2012 | .0302 | 3.69 | 4.75 |
| " | .2003 | .0311 | 3.82 | 6.50 |
| 29 | .2018 | - | - | 6.00 |

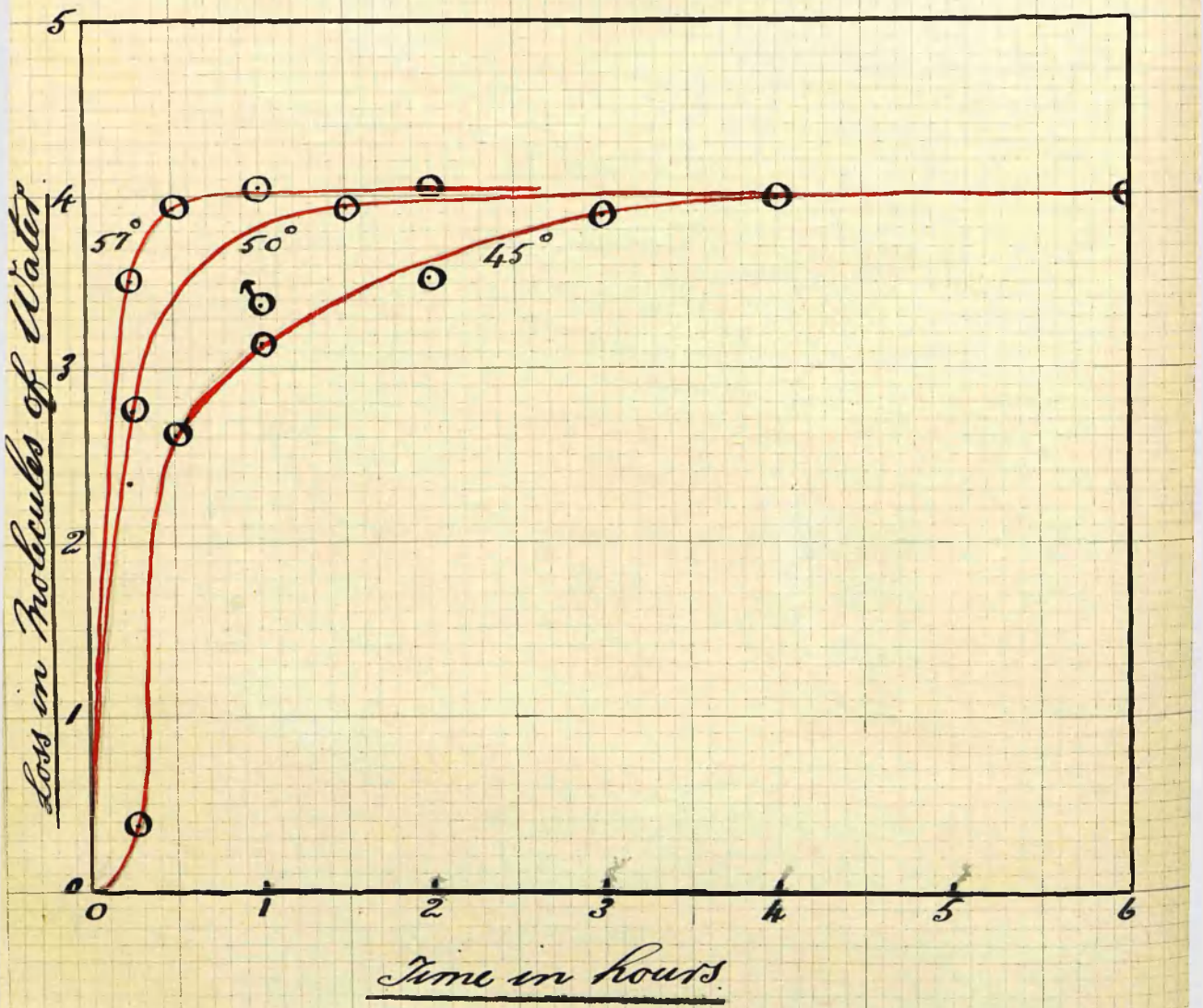
Examination of Fig.II and of the data given shows conclusively that copper potassium sulphate on dehydration forms a dehydrate $CuSO_4$, $K_2SO_4$, $2H_2O$, and that no other hydrate intermediate in water content between this and the hexahydrate exists. The presence of the induction lag is only slightly exhibited here, in the loss of rather more than four molecules of water, and, in the case of the readings at 32°C., in the curve passing through the first three points not cutting the origin.

# Fig III.

## Dehydration curves of Copper Ammonium Sulphate.

at

57°C., 50°C., and 45°C.



In Table II are given the data from which the curves in Fig. III were constructed.

TABLE II.

Copper Ammonium Sulphate.

| Temp. °C. | Wt. of salt taken. gm. | Loss in Wt. gm. | Loss in mols. of water. | Time. hrs. |
|---|---|---|---|---|
| 57 | .1500 | .0237 | 3.51 | 0.25 |
| " | .1500 | .0265 | 3.92 | 0.50 |
| " | .1497 | .0275 | 4.04 | 1.00 |
| " | .1495 | .0272 | 4.02 | 2.00 |
| 50 | .1515 | .0187 | 2.75 | 0.25 |
| " | .1496 | .0227 | 3.37 | 1.00 |
| " | .1500 | .0267 | 3.95 | 1.50 |
| " | .1500 | .0270 | 3.99 | 6.00 |
| 45 | .1506 | .0025 | 0.37 | 0.25 |
| " | .1506 | .0177 | 2.61 | 0.50 |
| " | .1534 | .0217 | 3.15 | 1.00 |
| " | .1517 | .0240 | 3.52 | 2.00 |
| " | .1498 | .0263 | 3.88 | 3.00 |
| " | .1495 | .0268 | 3.98 | 4.00 |
| " | .1509 | .0267 | 3.93 | 7.00 |
| " | .1495 | .0268 | 3.98 | 12.00 |
| " | .1529 | .0276 | 3.99 | 15.00 |
| " | .1529 | .0273 | 3.97 | 65.00 |

These figures show that copper ammonium sulphate on dehydration yields a dihydrate $CuSO_4$, $(NH_4)_2SO_4$, $2H_2O$. In Fig. IV is given the dehydration curve of copper ammonium sulphate, obtained by exposing a small weighed quantity of the salt over conc. sulphuric acid in an unevacuated desiccator for a period of more than a month. The data

## Dehydration curve of Copper Ammonium Sulphate in Desiccator.

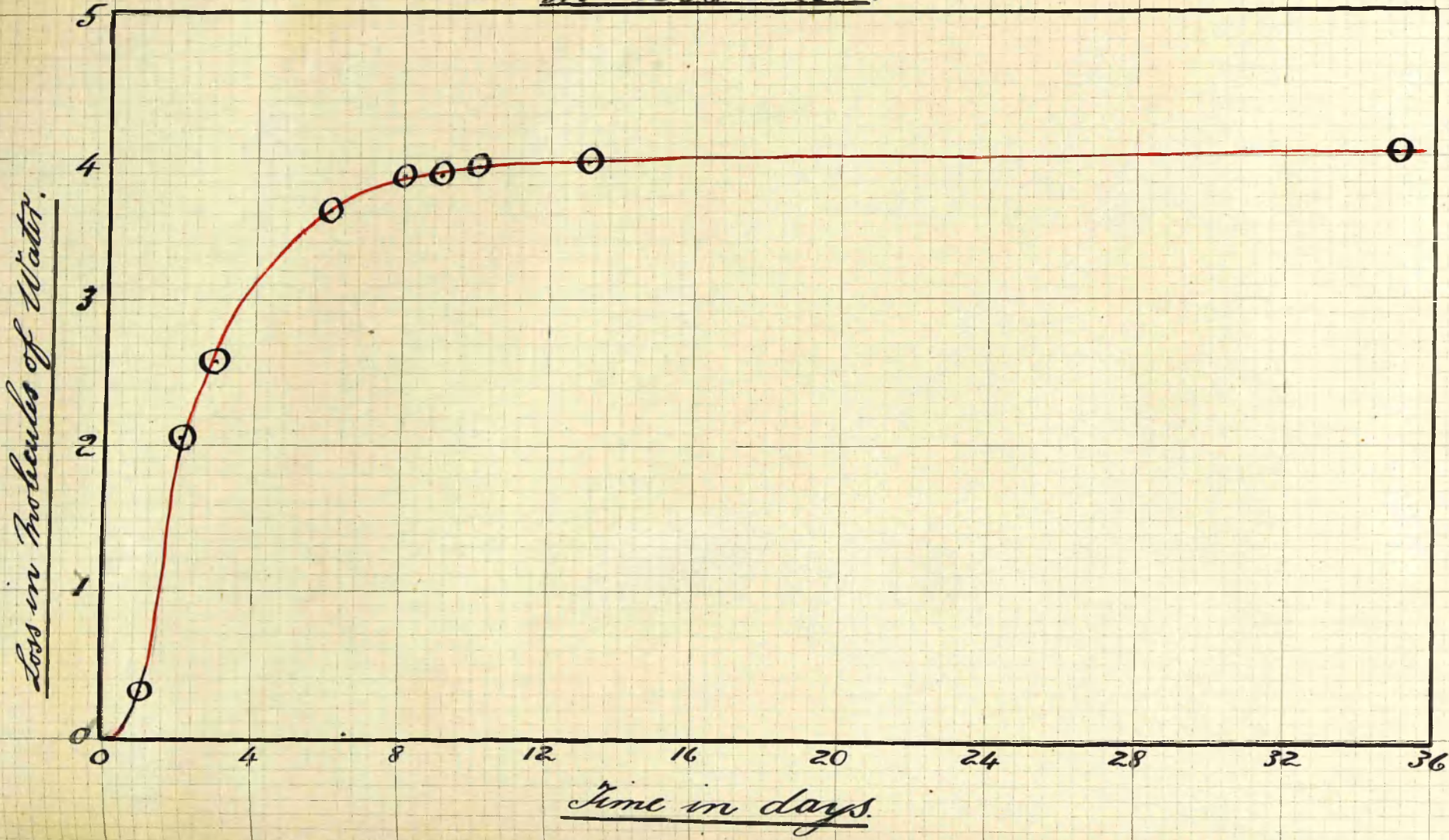



Fig. IV.

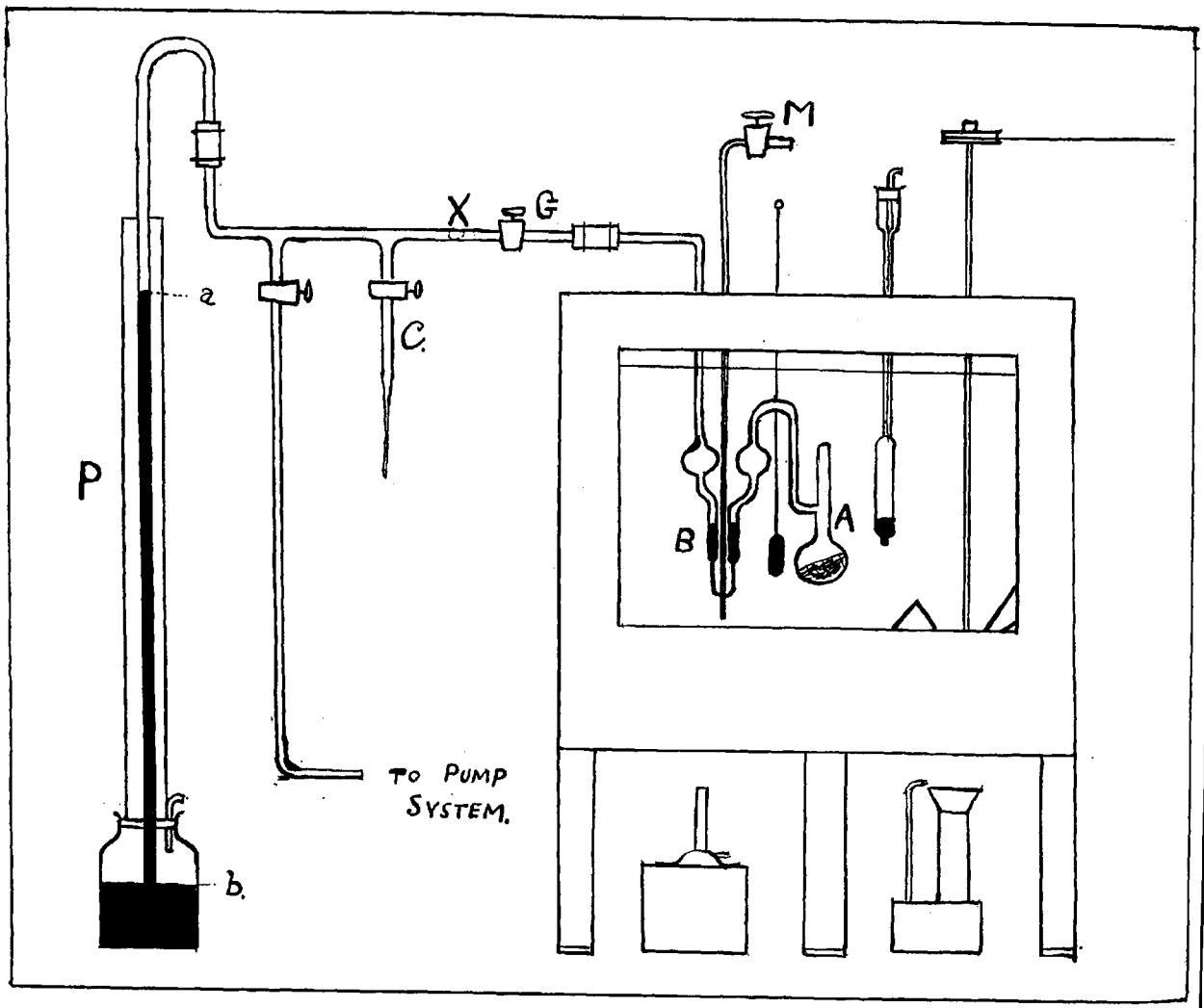
from which the curve is constructed are given in the following table.

TABLE III.

| Wt. of salt. gm. | Loss in Wt. gm. | Loss in mols. of water. | Time. Days. |
|---|---|---|---|
| .1928 | - | - | 0 |
| .1899 | .0027 | 0.31 | 1 |
| .1754 | .0174 | 2.05 | 2 |
| .1704 | .0224 | 2.58 | 3 |
| .1614 | .0314 | 3.62 | 6 |
| .1592 | .0336 | 3.87 | 8 |
| .1592 | .0336 | 3.87 | 9 |
| .1586 | .0342 | 3.94 | 10 |
| .1582 | .0346 | 3.98 | 13 |
| .1576 | .0352 | 4.02 | 35 |

The period of lag is again noticeable on this curve.

# Fig. V.



## Measurement of Dissociation Pressure.

Method and Apparatus. The apparatus employed is sketched in Fig.V. It is a slight modification of the apparatus used by Caven and Sand[14] in their work on the dissociation pressures of the alkali bicarbonates (J.C.S., 1911, 99, 1359), and closely resembled the tensimeter described by Johnston[15] (Z. Physik. Chem., 1908, 62, 333).

Its use depended on balancing the pressure developed by the hydrate on one side of a mercury gauge, B, by air, admitted to the other, whose presence was independently measured by means of a manometer, P, connected with the apparatus. The air was admitted through the tube C, which is drawn out to a fine capillary, by turning the stop-cork shewn. The gauge B was filled with mercury after the evacuation of the apparatus, by means of the stop-cork M. The stop-cork G was introduced for convenience in manipulation. The flask, A, of about 50 cc. capacity contained the hydrate mixture (about 20% of the lower hydrate was used - eight grammes of hexahydrate to two grammes of the lower hydrate). The stem of the flask was sealed off in the blowpipe after the introduction of the material. Two tensimeters were used. The second one is not shown in the figure, since it was placed behind the first, and slightly to the side of it to allow the gauge to be seen. The connecting tube of the second tensimeter was bent at right angles and entered the main tube connecting the manometer with the first tensimeter at the point X. The tensimeters were immersed in water in a large well stirred thermostat heated by gas burners. The temperature could be maintained within 0.2°C of any desired temperature by means of a mercury toluene thermoregulator of the usual type.

Two thermometers were used, a 0°-50°C and a 50°C-100°C., each graduated in tenths of a degree. Each was standardized against a Kew thermometer. The level of the mercury in the manometer P was read by means of a telescope against a millimetre scale placed in close contact with the manometer tube. The level of the mercury in the reservoir was obtained by reading the position of the top end of a needle of known length, whose point just made contact with the mercury surface in the reservoir. By determining once for all the rise in the mercury level at "b" for a given fall at "a" it was possible to determine the pressure exerted by the air admitted through C by two readings of the mercury level at "a" only - one when the barometer tube was completely evacuated and the other when the small amount of air was present. In the apparatus used the level of the mercury in the reservoir rose 1 mm. when the mercury in the barometer tube fell 40 mm. In taking a pressure reading the barometer was completely evacuated and the reading on the barometer scale noted. The stop-cork C was then opened and air was gradually admitted to the apparatus until the mercury levels in the gauge B appeared the same when seen against a small scale. The level of the mercury in the barometer tube P was again read, and the difference between this reading and the previous one gave the pressure of the air to the left of the mercury gauge B, which is equal in value to the dissociation pressure of the hydrate in A. The mercury surfaces in the gauge could be adjusted level within 0.1 mm., and the mercury levels in P could be read to 0.1 mm. Hence the total error in the pressure readings was $\pm$0.3 mm.

To evacuate the apparatus a rotary air pump manufactured

by Leybold, Cologne, was used. This pump was specified to give a vacuum of 0.01mm. Later a mercury vapour jet pump was used, giving a vacuum of 0.001mm. These pumps could be tested by means of a MacLeod gauge, and were always found to give a vacuum of at least 0.01mm.

The results of the dissociation pressure measurements have been expressed by formulae of the type :

$$\log p = a + \frac{b}{T} - \frac{c}{T^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where p is the pressure in millimetres of mercury, at the absolute temperature T, and a, b and c are empirical constants. These were obtained by substituting in (1) the pressure values observed at three different temperatures and solving the three resultant simultaneous equations for a, b and c.

On plotting the logarithms of the pressures against the reciprocals of the corresponding absolute temperatures slightly curved lines are obtained. These lines would of course be straight if the results could be expressed by formulae of the type:

$$\log p = a + \frac{b}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The term $\frac{c}{T^2}$ therefore is necessary to express this deviation. It is obvious from consideration of the well-known van't Hoff expression:

$$\frac{\partial \log p}{\partial T} = \frac{Q_v}{RT^2}$$

which on integration gives :

$$\log p = \frac{Q_v}{RT} + \text{constant, i.e. } = a + \frac{b}{T}$$

$$\text{where } b = \frac{Q_v}{R}$$

that this deviation from linearity shows that the heat of hydration is not constant but decreases with increasing temperature.

The formulae thus obtained are useful for comparison purposes. They also indicate the general consistency of a series of measurements, by comparison of the calculated values with those observed. They are also useful for calculating the heat absorbed in the dissociation.

The heat in calories $Q_T$ evolved per mole of $H_2O$ in the hydration of the lower hydrate at any absolute temperature T is given by an expression of the form :-

$$Q_T = 2.303\ R \left\{\frac{2c}{T} - b\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where b and c are the second and third constants in equation (1) and R is the gas constant. Equation (5) is obtained as follows:

By the van't Hoff isochore $\frac{d\ (\log_e p)}{dT} = \frac{Q_v}{RT^2}$

now $\frac{d(\log_{10} p)}{dT} = \frac{d\left\{a + \frac{b}{T} - \frac{c}{T^2}\right\}}{dT} = \frac{2c}{T^3} - \frac{b}{T^2}$

but $2.303\ \frac{d(\log_{10} p)}{dT} = \frac{Q_v}{RT^2}$

$$\therefore \quad Q_T = 2.303R\left\{\frac{2c}{T} - b\right\}$$

# PRESSURE MEASUREMENTS.

## I. DOUBLE SULPHATES.

# 1. DOUBLE SULPHATES FORMING DIHYDRATES ON DISSOCIATION.

## COBALT POTASSIUM SULPHATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 44.17 | 43.91 |
| | $\%H_2O$ | 24.82 | 24.72 |

### Hydrate Formation.

See page 6. for further details. The salt forms a dihydrate.

### Pressure Measurements.

$$CoSO_4K_2SO_46H_2O \rightleftharpoons CoSO_4K_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 26.5 | 7.2 | - | 7.0 |
| 32.8 | 11.6 | - | 11.6 |
| 39.6 | 19.2 | - | 19.8 |
| 45.7 | 30.6 | - | 30.7 |
| 51.1 | 44.2 | - | 44.3 |
| 57.0 | 64.2 | - | 65.1 |
| 60.6 | 81.6 | - | 81.7 |
| 66.3 | 114.6 | - | 115.1 |
| 76.3 | 201.3 | - | 201.3 |
| 66.2 | - | 113.4 | 114.3 |
| 54.0 | - | 53.5 | 53.6 |
| 40.3 | - | 20.8 | 20.8 |
| 34.3 | - | 13.9 | 13.2 |
| 27.6 | - | 8.3 | 7.7 |
| 31.5 | 10.5 | - | 10.6 |
| 44.4 | 27.5 | - | 28.2 |
| 50.1 | 41.0 | - | 41.5 |
| 59.9 | 78.1 | - | 78.3 |

### Formula.

The numbers in the last column were calculated by means of the formula:

$$\log p = 6.764 - \frac{265.7}{T} - \frac{451,350}{T^2}$$

The heat absorbed in the dissociation per gramme-molecule of water vapour at 50°C., ($Q_{50}$) = 14,000 calories.

## Cobalt Rubidium Sulphate.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 36.23 | 36.43 |
| | $\%H_2O$ | 20.30 | 20.48 |

### Hydrate Formation.

The salt exhibits the same phenomena as the potassium salt, finally yielding a dihydrate at a temperature a little over 80°C.

### Pressure Measurements.

$$CoSO_4Rb_2SO_46H_2O \rightleftharpoons CoSO_4Rb_2SO_42H_2O + 4H_2O$$

| | Pressure in mm. of mercury. | | |
|---|---|---|---|
| Temp. °C. | Rising. | Falling. | Calculated. |
| 28.4 | 4.3 | - | 4.3 |
| 33.3 | 6.8 | - | 6.4 |
| 38.4 | 9.7 | - | 9.9 |
| 45.3 | 16.3 | - | 16.5 |
| 52.6 | 26.9 | - | 27.7 |
| 58.9 | 41.7 | - | 41.4 |
| 65.1 | 59.9 | - | 60.2 |
| 76.1 | 112.2 | - | 111.0 |
| 53.3 | - | 28.8 | 28.8 |
| 35.8 | - | 8.0 | 8.0 |
| 27.4 | - | 4.1 | 4.0 |

### Formula.

$$\log p = 3.740 + \frac{1594}{T} - \frac{762,735}{T^2}$$

$Q_{50}$ = 14,300 calories.

## Cobalt Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 31.03 | 30.74 |
| $\%H_2O$ | 17.44 | 17.29 |

### Hydrate Formation.

Yields a dihydrate about 80°C., behaving like the potassium salt.

### Pressure Measurements.

$$CoSO_4Cs_2SO_46H_2O \rightleftharpoons CoSO_4Cs_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 29.2 | 5.1 | - | 4.9 |
| 41.0 | 12.2 | - | 12.5 |
| 47.0 | 19.6 | - | 19.4 |
| 53.8 | 31.3 | - | 31.2 |
| 60.2 | 47.6 | - | 47.6 |
| 75.0 | 118.6 | - | 117.0 |
| 66.2 | - | 70.1 | 69.7 |
| 58.8 | - | 44.0 | 43.3 |
| 51.6 | - | 26.5 | 26.8 |
| 43.1 | - | 15.0 | 14.8 |

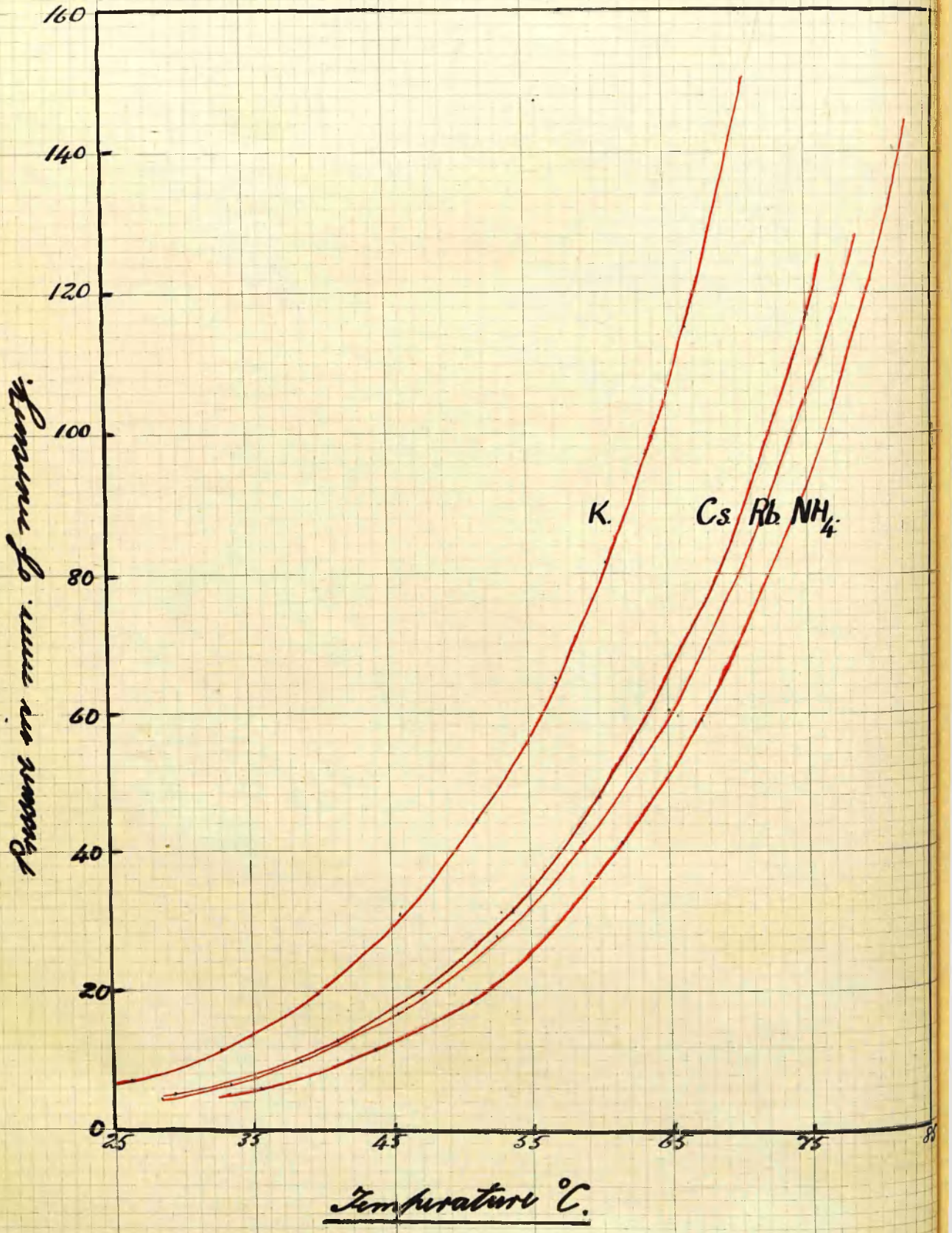
### Formula.

$$\log p = 8.164 - \frac{1221}{T} - \frac{313,270}{T^2}$$

$$Q_{50} = 14,400 \text{ Calories.}$$

# Fig VI.

## Dissociation Pressures of Cobalt Double Sulphates.



## Cobalt Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 48.34 | 48.61 |
| $\%H_2O$ | 26.93 | 27.17 |

### Hydrate Formation.

The salt behaves like the other cobalt salts forming a reddish pink hydrate at 80°C.

### Pressure Measurements.

$$CoSO_4(NH_4)_2SO_4 6H_2O \rightleftharpoons CoSO_4(NH_4)_2SO_4 2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calc. |
|---|---|---|---|
| 35.3 | 5.7 | - | 6.0 |
| 43.8 | 11.8 | - | 11.5 |
| 50.7 | 19.3 | - | 19.2 |
| 61.7 | 41.2 | - | 41.2 |
| 67.3 | 58.7 | - | 58.8 |
| 82.2 | 140.9 | - | 140.6 |
| 54.0 | - | 25.0 | 24.6 |
| 57.1 | - | 15.5 | 15.1 |
| 37.5 | - | 7.2 | 7.2 |

### Formula.

$$\log p = 7.600 - \frac{843.4}{T} - \frac{388,340}{T^2}$$

$$Q_{50} = 14,800 \text{ Calories.}$$

The cobalt double sulphate dissociation pressure curves are shown in Fig. VI.

## Zinc Potassium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 42.97 | 43.25 |
| $\%H_2O$ | 24.20 | 24.36 |

### Hydrate Formation.

This salt first loses water on heating to a temperature of 70°C. when the anhydrous salt is produced. After several rehydrations, a loss of four molecules of water occurs. The dihydrate thus produced is ill defined and readily loses more water. The same phenomena occur with the other zinc double sulphates, all forming comparatively unstable dihydrates when heated to temperatures about 70°C.

### Pressure Measurements.

$$ZnSO_4K_2SO_46H_2O \rightleftharpoons ZnSO_4K_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calc. |
|---|---|---|---|
| 35.9 | 14.1 | - | 14.1 |
| 38.7 | 16.6 | - | 17.2 |
| 49.2 | 34.2 | - | 35.2 |
| 57.2 | 59.6 | - | 59.3 |
| 63.4 | 87.1 | - | 87.1 |
| 52.3 | - | 44.4 | 43.2 |
| 45.4 | - | 27.3 | 27.4 |
| 38.1 | - | 16.2 | 16.4 |
| 16.2 | - | 3.6 | 3.1 |

### Formula.

$$\log p = 10.834 - \frac{2992}{T}$$

$$Q_{50} = 13{,}800 \text{ Calories.}$$

## Zinc Rubidium Sulphate.

**Analysis.**

| | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 36.30 | 36.64 |
| $\%H_2O$ | 20.08 | 20.15 |

**Pressure Measurements.**

$$ZnSO_4Rb_2SO_46H_2O = ZnSO_4Rb_2SO_42H_2O + 4H_2O$$

| Temp.°C. | Pressure in mm. of mercury. Rising. | Falling. | Calc. |
|---|---|---|---|
| 33.3 | 3.6 | - | 4.0 |
| 36.1 | 5.3 | - | 5.3 |
| 41.2 | 7.9 | - | 7.7 |
| 47.6 | 13.6 | - | 13.7 |
| 55.6 | 25.2 | - | 24.9 |
| 64.7 | 46.0 | - | 45.9 |
| 77.5 | 100.2 | - | 100.2 |
| 81.5 | 125.1 | - | 125.8 |
| 70.2 | - | 65.0 | 65.5 |
| 66.2 | - | 51.7 | 51.2 |
| 55.3 | - | 25.0 | 24.4 |
| 46.8 | - | 13.3 | 12.9 |

**Formula.**

$$\log p = 3.739 + \frac{1804}{T} - \frac{845,640}{T^2}$$

$$Q_{50} = 15,600 \text{ calories.}$$

## Zinc Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 30.88 | 30.42 |
| $\%H_2O$ | 17.29 | 17.13 |

### Pressure Measurements.

$$ZnSO_4Cs_2SO_46H_2O \rightleftharpoons ZnSO_4Cs_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 34.4 | 5.9 | - | 5.2 |
| 41.0 | 9.3 | - | 9.3 |
| 46.7 | 15.0 | - | 14.8 |
| 53.4 | 25.2 | - | 24.5 |
| 59.8 | 38.4 | - | 38.4 |
| 70.7 | 76.4 | - | 76.2 |
| 60.8 | - | 41.1 | 40.9 |
| 44.3 | - | 12.7 | 12.2 |
| 34.4 | - | 5.4 | 5.2 |

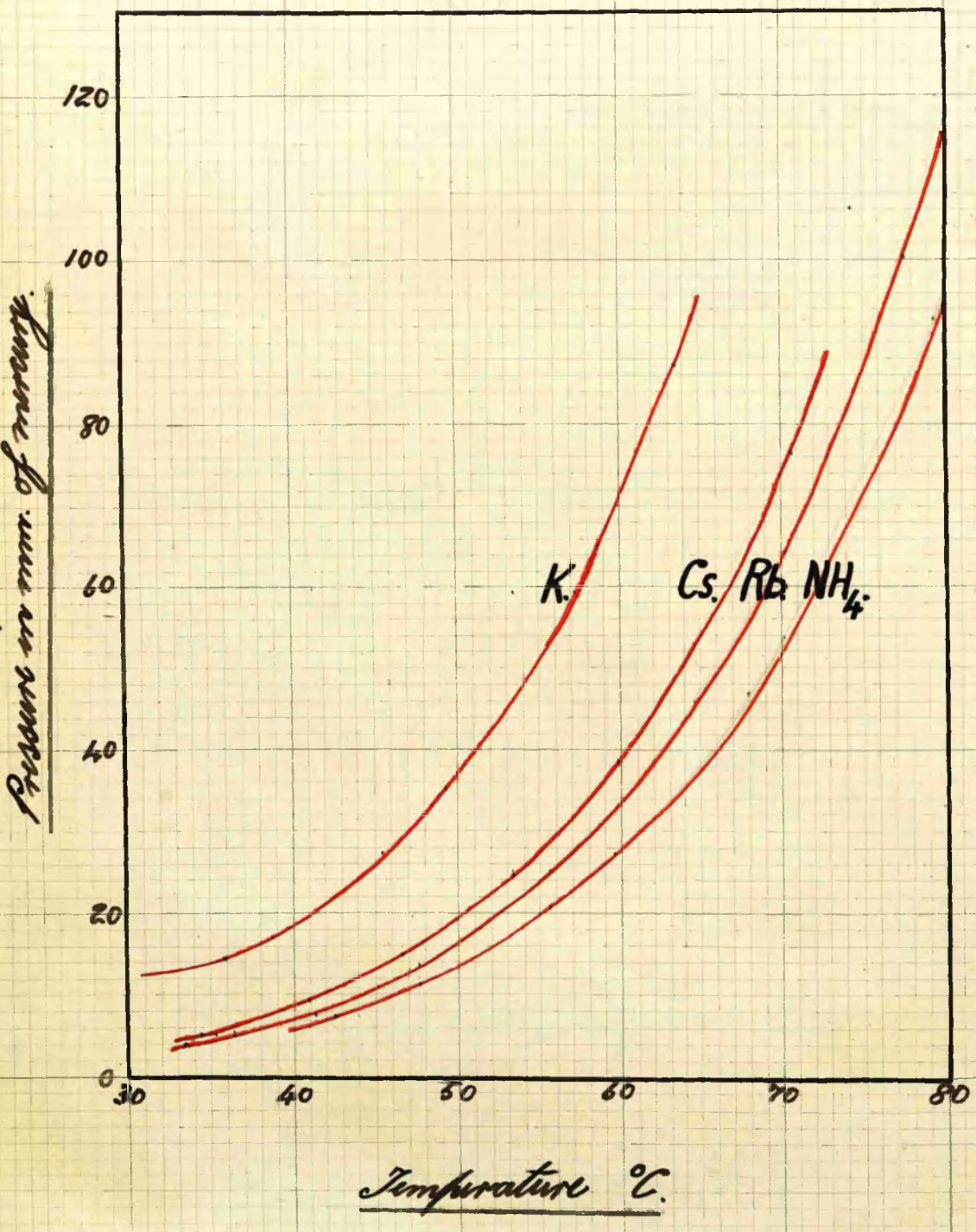
### Formula.

$$\log p = 1.733 + \frac{3135}{T} - \frac{1,059,814}{T^2}$$

$$Q_{50} = 15,500 \text{ calories.}$$

# Fig VII

## Dissociation Pressure Curves of the Zinc Double Sulphates.



## Zinc Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 47.93 | 47.84 |
| $\%H_2O$ | 26.80 | 26.90 |

### Pressure Measurements.

$$ZnSO_4, (NH_4)_2SO_4, 6H_2O \rightleftharpoons ZnSO_4, (NH_4)_2SO_4, 2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 42.5 | 7.4 | - | 7.6 |
| 47.6 | 10.9 | - | 11.3 |
| 55.6 | 20.5 | - | 20.5 |
| 59.7 | 26.4 | - | 27.4 |
| 68.0 | 46.4 | - | 46.8 |
| 70.2 | 53.7 | - | 53.8 |
| 79.4 | 93.1 | - | 92.7 |
| 64.7 | - | 37.9 | 37.8 |
| 56.5 | - | 22.0 | 21.8 |
| 45.0 | - | 9.3 | 9.3 |
| 40.4 | - | 6.6 | 6.4 |
| 30.7 | - | 3.2 | 2.8 |

### Formula.

$$\log p = 5.636 + \frac{471.5}{T} - \frac{622,000}{T^2}$$

$$Q_{50} = 15,400 \text{ calories.}$$

The curves for the zinc double sulphates are reproduced in Fig. VII.

## Nickel Potassium Sulphate.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 44.19 | 43.94 |
| | $\%H_2O$ | 24.65 | 24.67 |

### Hydrate Formation.

When first heated this salt begins to lose water at 105°C and forms the yellow anhydrous salt. Careful heating at 80°C. after rehydration results in the formation of a yellowish green dihydrate, which is stable up to 100°C. The same phenomena were observed with the other nickel double sulphates, all forming dihydrates.

### Pressure Measurements.

$$NiSO_4K_2SO_46H_2O \rightleftharpoons NiSO_4K_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 33.8 | 6.2 | - | 6.2 |
| 45.1 | 14.6 | - | 15.1 |
| 55.8 | 31.2 | - | 31.3 |
| 64.8 | 54.6 | - | 53.7 |
| 76.2 | 98.1 | - | 98.2 |
| 66.5 | - | 59.6 | 59.0 |
| 60.8 | - | 42.8 | 42.4 |
| 48.6 | - | 19.4 | 19.3 |

### Formula.

$$\log p = 0.981 + \frac{3329}{T} - \frac{1,039,000}{T^2}$$

$$Q_{50} = 14,100 \text{ calories.}$$

## Nickel Rubidium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 35.87 | 36.24 |
| $\%H_2O$ | 20.50 | 20.38 |

### Pressure Measurements.

$$NiSO_4Rb_2SO_46H_2O \rightleftharpoons NiSO_4Rb_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 32.5 | 3.0 | - | 3.0 |
| 40.1 | 5.5 | - | 5.3 |
| 49.6 | 10.5 | - | 10.7 |
| 58.3 | 19.9 | - | 19.5 |
| 74.8 | 55.7 | - | 56.0 |
| 67.1 | - | 35.2 | 34.7 |
| 51.9 | - | 12.9 | 12.6 |
| 34.4 | - | 3.5 | 3.4 |

### Formula.

$$\log p = 10.563 - \frac{2937}{T} + \frac{44,740}{T^2}$$

$$Q_{50} = 14,400 \text{ calories.}$$

## Nickel Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 31.03 | 30.75 |
| $\%H_2O$ | 17.53 | 17.30 |

### Pressure Measurements.

$$NiSO_4Cs_2SO_46H_2O \rightleftharpoons NiSO_4Cs_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Calculated. |
|---|---|---|
| 35.0 | 4.8 | 4.8 |
| 44.2 | 9.0 | 9.3 |
| 48.7 | 12.6 | 12.9 |
| 55.9 | 18.9 | 20.2 |
| 65.7 | 35.4 | 34.9 |
| 82.0 | 75.2 | 74.1 |

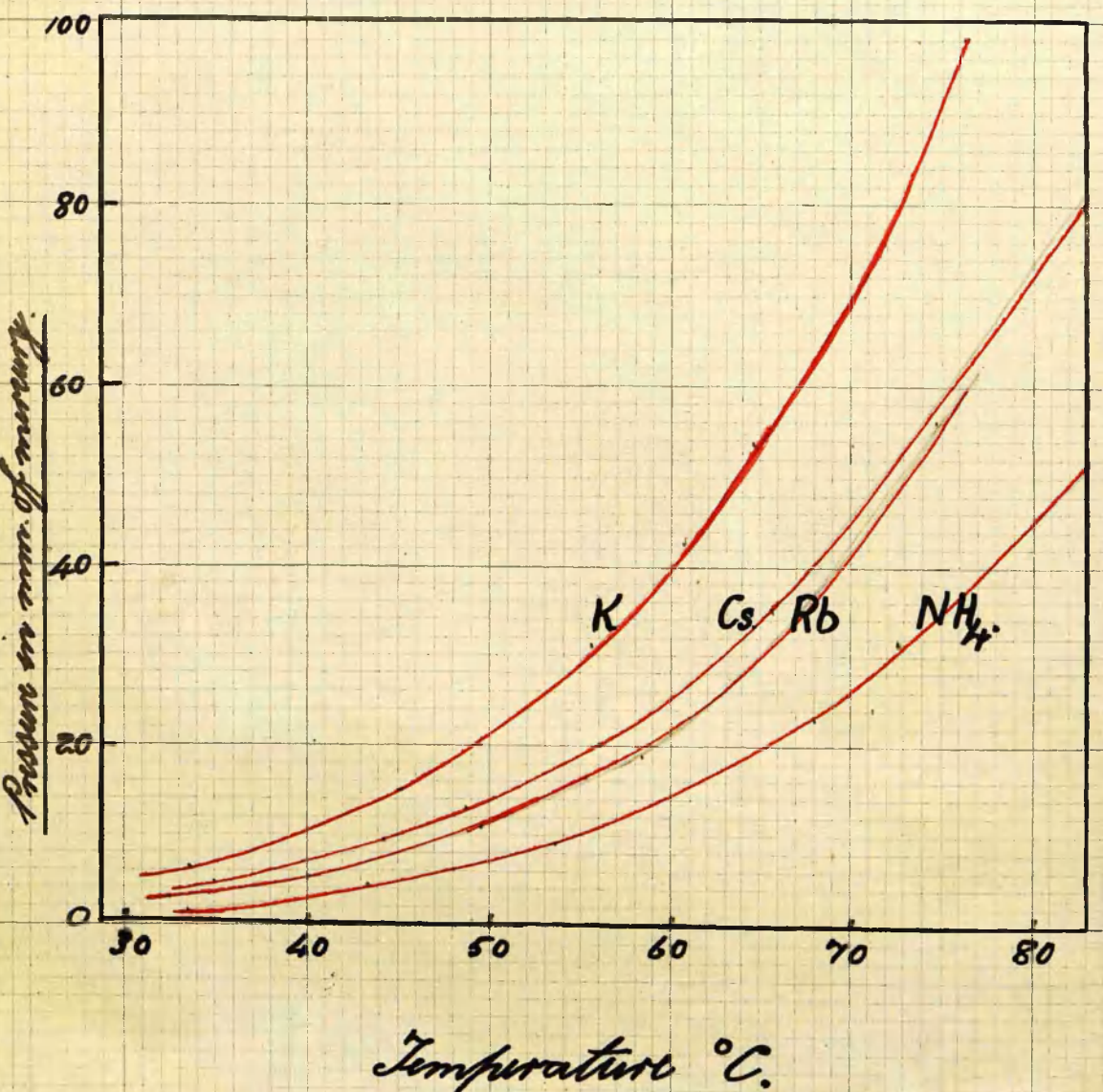
### Formula.

$$\log p = -1.730 + \frac{4798}{T} - \frac{1,249,600}{T^2}$$

$$Q_{50} = 13,400 \text{ calories.}$$

Fig. VIII

## Dissociation Pressure Curves of the Nickel Double Sulphates.



## Nickel Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 48.64 | 48.68 |
| $\%H_2O$ | 27.30 | 27.38 |

Pressure Measurements.

$$NiSO_4(NH_4)_2SO_4 6H_2O \rightleftharpoons NiSO_4(NH_4)_2SO_4 2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calc. |
|---|---|---|---|
| 33.5 | 1.6 | - | 1.8 |
| 43.2 | 4.1 | - | 4.1 |
| 53.7 | 9.2 | - | 9.2 |
| 68.0 | 24.3 | - | 23.1 |
| 72.8 | 31.9 | - | 31.8 |
| 64.1 | - | 18.6 | 18.7 |
| 48.2 | - | 5.7 | 6.1 |
| 40.9 | - | 3.4 | 3.3 |

Formula.

$$\log p = 2.370 + \frac{2437}{T} - \frac{946,400}{T^2}$$

$$Q_{50} = 15,400 \text{ calories.}$$

The nickel double sulphate pressure curves are reproduced in Fig. VIII.

## Cadmium Potassium Sulphate.

The salt $CdSO_4$, $K_2SO_4$, $6H_2O$ does not appear to exist. Tutton (J.C.S. 1893, 63, 407) was unable to prepare it.

Attemps to prepare the salt by the method given by Gmelin-Kraut, Vol. IV, p. 157, yielded substances giving very variable analytical figures, approximating extremely roughly to the composition of the dihydrate $CdSO_4$, $K_2SO_4$, $2H_2O$.

The dihydrate is a quite stable salt, however, and in view of the high dissociation pressures of the rubidium and caesium cadmium sulphate hexahydrates, and the consequent still higher dissociation pressure which would be possessed by the potassium salt, did it exist, the non-existence of cadmium potassium hexahydrate is explicable.

## Cadmium Rubidium Sulphate.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 33.18 | 32.92 |
| | $\%H_2O$ | 18.22 | 18.53 |

### Hydrate Formation.

The salt effloresces when exposed to air forming the dihydrate, which is stable in air up to a temperature of 100°C.

### Pressure Measurements.

$$CdSO_4, Rb_2SO_4, 6H_2O \rightleftharpoons CdSO_4, Rb_2SO_4, 2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 28.0 | 23.1 | - | 23.1 |
| 34.6 | 35.0 | - | 34.8 |
| 40.1 | 47.8 | - | 47.8 |
| 45.4 | 63.9 | - | 64.0 |
| 50.9 | 85.1 | - | 85.1 |
| 56.4 | 111.8 | - | 111.7 |
| 61.7 | 142.5 | - | 142.6 |
| 67.5 | 184.5 | - | 184.5 |
| 56.4 | - | 111.7 | 111.7 |
| 47.2 | - | 69.6 | 70.5 |
| 42.1 | - | 53.1 | 53.5 |
| 37.9 | - | 42.6 | 42.3 |
| 32.6 | - | 31.2 | 31.0 |

Formula.

$$\log p = 4.759 + \frac{471.2}{T} - \frac{449,370}{T^2}$$

$$Q_{50} = 10,500 \text{ calories.}$$

Attention is drawn to the fact that the vapour pressures of the rubidium salt are higher than those of the caesium salt.

## Cadium Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 28.76 | 28.32 |
| $\%H_2O$ | 15.60 | 15.94 |

### Dehydration.

The caesium salt is more stable in air than the corresponding rubidium salt, but it too effloresces, yielding a dihydrate stable up to 100°C.

### Pressure Measurements.

$$CdSO_4Cs_2SO_46H_2O \rightleftharpoons CdSO_4Cs_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 25.7 | 17.2 | - | 17.9 |
| 32.0 | 28.2 | - | 27.4 |
| 34.5 | 31.6 | - | 32.0 |
| 40.2 | 46.1 | - | 45.2 |
| 46.1 | 62.8 | - | 62.8 |
| 51.8 | 84.0 | - | 84.6 |
| 61.0 | 130.1 | - | 130.7 |
| 64.4 | 151.3 | - | 151.4 |
| 48.4 | - | 72.2 | 71.5 |
| 33.6 | - | 30.2 | 30.3 |
| 26.8 | - | 19.5 | 19.4 |

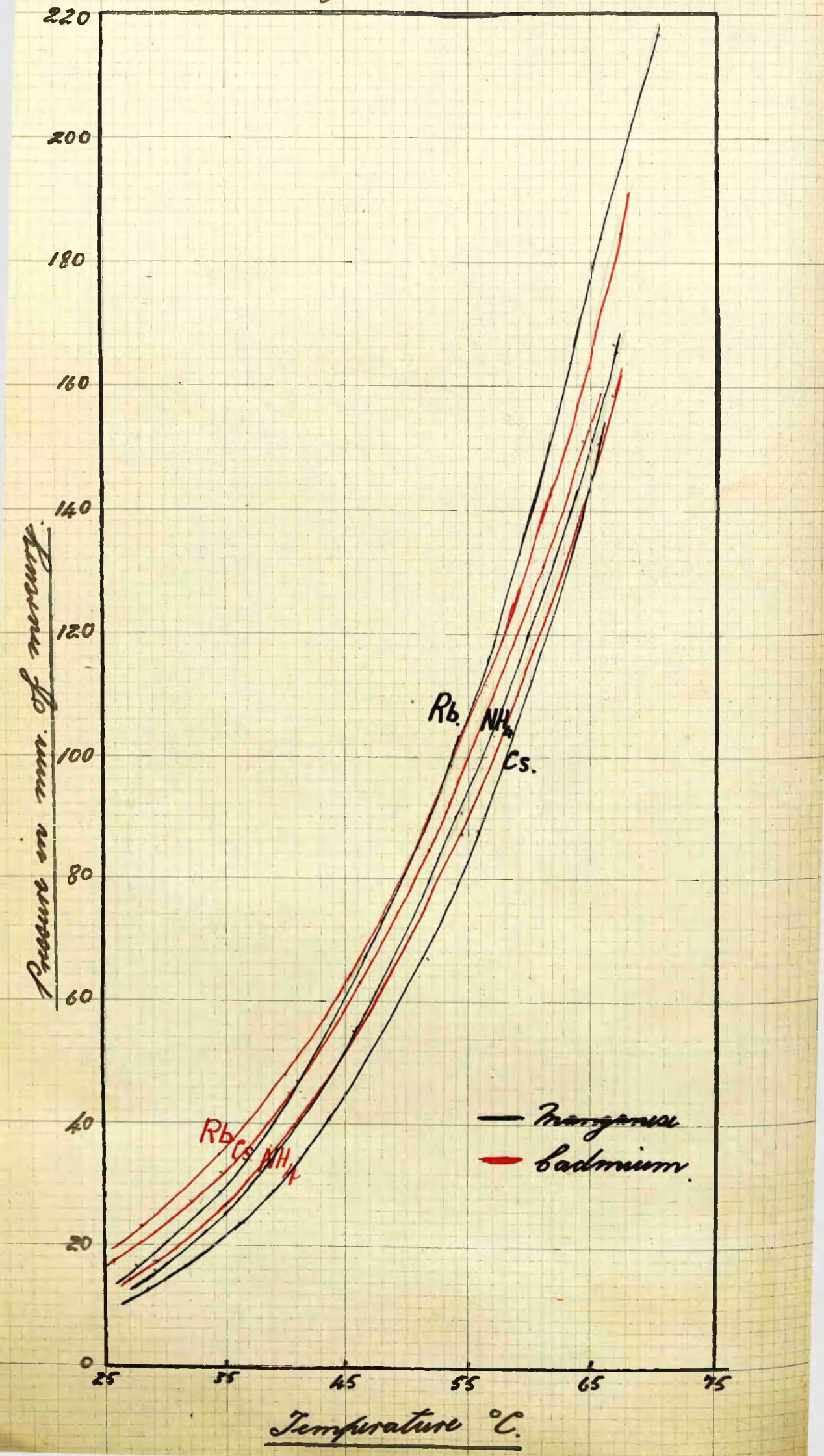
### Formula.

$$\log p = 1.245 + \frac{2735}{T} - \frac{816,170}{T^2}$$

$$Q_{50} = 10,600 \text{ calories.}$$

# Fig IX

## Cadmium & Manganese Double Sulphates



## Cadmium Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 42.93 | 42.82 |
| $\%H_2O$ | 23.97 | 24.11 |

### Hydrate Formation.

The salt effloresces slightly in air, and readily forms the dihydrate when slightly heated.

### Pressure Measurements.

$$CdSO_4,(NH_4)_2SO_4.6H_2O \rightleftharpoons CdSO_4,(NH_4)_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury, Rising. | Calculated. |
|---|---|---|
| 29.1 | 16.8 | 17.2 |
| 34.9 | 26.4 | 26.4 |
| 45.8 | 54.3 | 53.7 |
| 54.3 | 87.7 | 87.1 |
| 66.7 | 158.3 | 159.2 |

### Formula.

$$\log p = -1.131 + \frac{4485}{T} - \frac{1,139,000}{T^2}$$

$$Q_{50} = 11,700 \text{ calories.}$$

The cadmium salt curves are reproduced in Fig. IX.

## Manganese Potassium Sulphate.

As in the case of cadmium, the corresponding potassium salt $MnSO_4K_2SO_46H_2O$ does not appear to exist. (Tutton, loc. cit.

## Manganese Rubidium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 36.75 | 36.51 |
| $\%H_2O$ | 20.35 | 20.55 |

### Dehydration.

The salt loses four molecules of water when heated to 40°C. The dihydrate thus formed, when exposed to air, does not rehydrate itself.

### Pressure Measurements.

$$MnSO_4,Rb_2SO_4,6H_2O \rightleftharpoons MnSO_4,Rb_2SO_42H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Calculated. |
|---|---|---|
| 27.5 | 16.7 | 16.3 |
| 34.4 | 28.7 | 28.6 |
| 41.0 | 45.8 | 46.3 |
| 46.7 | 67.4 | 67.3 |
| 53.4 | 98.5 | 98.5 |
| 70.7 | 216.7 | 216.8 |

### Formula.

$$\log p = -7.084 + \frac{8419}{T} - \frac{1,781,000}{T^2}$$

$$Q_{50} = 13,000 \text{ calories.}$$

The dissociation pressure curve of manganese rubidium sulphate cuts the curves of both cadmium rubidium sulphate and cadmium caesium sulphate at temperatures of 42.5°C. and 49°C. respectively.

## Manganese Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 31.30 | 30.94 |
| $\%H_2O$ | 17.74 | 17.42 |

### Dehydration.

The salt loses four molecules of water when heated to about 40°C. The dihydrate when exposed to air at ordinary temperature does not rehydrate itself.

### Pressure Measurements.

$$MnSO_4,Cs_2SO_4,6H_2O \rightleftharpoons MnSO_4,Cs_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Calculated. |
|---|---|---|
| 28.5 | 13.9 | 12.8 |
| 36.4 | 23.9 | 23.9 |
| 43.8 | 39.7 | 40.6 |
| 51.7 | 69.8 | 67.0 |
| 55.8 | 88.3 | 87.7 |
| 65.4 | 152.3 | 151.0 |

### Formula.

$$\log p = 2.830 + \frac{2236}{T} - \frac{830,860}{T^2}$$

$$Q_{50} = 13,300 \text{ calories.}$$

## Manganese Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 48.96 | 49.11 |
| $\%H_2O$ | 27.80 | 27.65 |

### Hydrate Formation.

When heated between 30° and 40°C. the dihydrate is formed.

### Pressure Measurements.

$$MnSO_4,(NH_4)_2SO_4,6H_2O \rightleftharpoons MnSO_4,(NH_4)_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Calculated. |
|---|---|---|
| 29.1 | 16.2 | 15.9 |
| 34.9 | 25.2 | 25.4 |
| 45.8 | 55.0 | 55.0 |
| 54.3 | 91.6 | 90.8 |
| 66.7 | 166.4 | 166.7 |

### Formula.

$$\log p = -4.372 + \frac{6724}{T} - \frac{1,522,600}{T^2}$$

$$Q_{50} = 12,700 \text{ calories.}$$

The manganese salt curves are shewn in Fig. IX. Attention is drawn to the position of Caesium.

## Copper Potassium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 43.72 | 43.46 |
| $\%H_2O$ | 24.21 | 24.45 |

### Dehydration.

A dihydrate is formed when the salt is heated to 33°C. in air. Fuller details are given on page

### Pressure Measurements.

$$CuSO_4,K_2SO_4,6H_2O = CuSO_4,K_2SO_4,2H_2O + 4H_2O$$

| | Pressure in mm. of mercury. | | |
|---|---|---|---|
| Temp. °C. | Rising. | Falling. | Calculated. |
| 23.7 | 7.6 | - | 7.6 |
| 30.3 | 13.0 | - | 13.4 |
| 34.9 | 19.5 | - | 19.5 |
| 40.9 | 30.9 | - | 30.9 |
| 45.3 | 41.3 | - | 42.5 |
| 51.8 | 66.9 | - | 66.9 |
| 58.5 | 101.2 | - | 102.1 |
| 64.9 | 151.0 | - | 150.3 |
| 76.8 | 288.4 | - | 288.4 |
| 70.0 | - | 201.1 | 200.4 |
| 62.6 | - | 130.4 | 131.2 |
| 55.6 | - | 86.3 | 85.5 |
| 44.5 | - | 39.4 | 40.5 |
| 39.1 | - | 26.8 | 27.1 |
| 30.5 | - | 13.8 | 13.6 |
| 13.8 | - | 3.0 | 2.8 |
| 26.9 | 10.4 | - | 10.1 |
| 37.6 | 23.9 | - | 24.1 |
| 44.5 | 40.6 | - | 40.5 |

### Formula.

$$\log p = 4.574 + \frac{1251}{T} - \frac{696,500}{T^2}$$

$$Q_{50} = 14,000 \text{ calories.}$$

## Copper Rubidium Sulphate.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 35.63 | 35.91 |
| | $\%H_2O$ | 20.17 | 20.21 |

### Dehydration.

When the salt is heated to 55°C. in air, the dihydrate is formed, which is stable up to 100°C.

### Pressure Measurements.

$$CuSO_4,Rb_2SO_4,6H_2O \rightleftharpoons CuSO_4,Rb_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 29.8 | 8.3 | - | 8.3 |
| 34.7 | 12.5 | - | 12.5 |
| 39.5 | 18.3 | - | 18.6 |
| 45.4 | 28.0 | - | 29.0 |
| 49.4 | 38.4 | - | 38.8 |
| 54.7 | 55.8 | - | 55.8 |
| 59.9 | 77.7 | - | 78.2 |
| 70.1 | 145.2 | - | 145.2 |
| 62.7 | - | 93.1 | 92.9 |
| 55.0 | - | 57.3 | 56.9 |
| 50.3 | - | 41.6 | 41.2 |
| 43.2 | - | 24.5 | 24.7 |
| 35.9 | - | 14.2 | 13.9 |
| 30.2 | - | 8.9 | 8.6 |
| 20.3 | - | 3.6 | 3.5 |

### Formula.

$$\log p = 4.930 + \frac{1040}{T} - \frac{682,600}{T^2}$$

$$Q_{50} = 14,500 \text{ calories.}$$

## Copper Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 30.13 | 30.52 |
| $\%H_2O$ | 17.37 | 17.17 |

### Dehydration.

The salt loses its water of crystallisation completely at about 75°C. It exhibits the induction phenomenon however, and if rehydrated in air, and again heated, the dihydrate is formed at 60°C.

### Pressure Measurements.

$$CuSO_4,Cs_2SO_4,6H_2O \rightleftharpoons CuSO_4,Cs_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 23.7 | 1.6 | - | 1.9 |
| 30.3 | 3.7 | - | 4.1 |
| 34.9 | 5.7 | - | 6.6 |
| 40.9 | 10.8 | - | 11.5 |
| 51.8 | 28.6 | - | 28.6 |
| 58.5 | 44.2 | - | 45.9 |
| 64.9 | 68.3 | - | 69.0 |
| 77.8 | 138.0 | - | 138.0 |
| 71.3 | - | 99.8 | 99.5 |
| 66.9 | - | 77.4 | 77.1 |
| 55.6 | - | 37.6 | 37.6 |
| 50.8 | - | 26.8 | 26.4 |
| 41.6 | - | 14.3 | 12.5 |
| 30.5 | - | 5.5 | 4.3 |

### Formula.

$$\log p = -6.052 + \frac{8234}{T} - \frac{1,911,600}{T^2}$$

$$Q_{50} = 16,100 \text{ calories.}$$

## Copper Thallous Sulphate.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 24.97 | 24.88 |
| | $\%H_2O$ | 13.97 | 14.01 |

### Dehydration.

The salt dissociates forming a dihydrate when heated to 60°C. in air.

### Pressure Measurements.

$$CuSO_4,Tl_2SO_4,6H_2O \rightleftharpoons CuSO_4,Tl_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 29.8 | 6.1 | - | 6.1 |
| 34.7 | 9.3 | - | 9.4 |
| 39.5 | 13.5 | - | 14.0 |
| 45.4 | 22.3 | - | 22.2 |
| 54.7 | 43.1 | - | 43.0 |
| 59.9 | 61.1 | - | 60.5 |
| 70.2 | 114.6 | - | 114.0 |
| 62.8 | - | 72.9 | 72.6 |
| 55.0 | - | 43.8 | 44.1 |
| 50.3 | - | 32.2 | 31.8 |
| 43.2 | - | 18.7 | 18.9 |
| 35.9 | - | 10.0 | 10.2 |
| 30.2 | - | 6.4 | 6.4 |
| 20.3 | - | 2.7 | 2.6 |

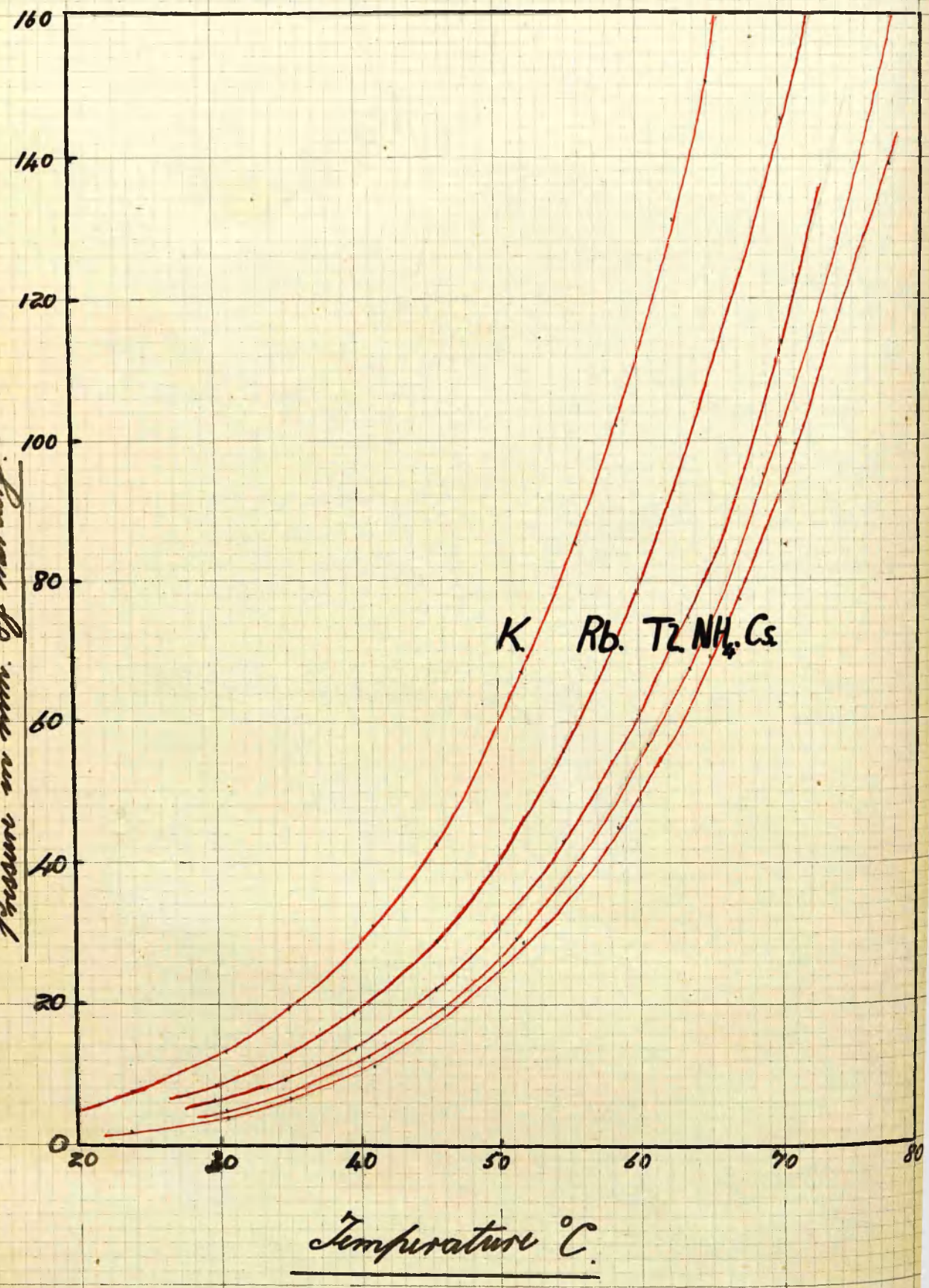
### Formula.

$$\log p = 4.204 + \frac{1485}{T} - \frac{762,600}{T^2}$$

$$Q_{50} = 14,800 \text{ calories.}$$

# Fig. X.

## Dissociation Pressure Curves of the Copper Double Sulphates.



## Copper Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| % $SO_4$ | 47.92 | 48.04 |
| % $H_2O$ | 27.14 | 27.05 |

### Dehydration.

See pp. The salt dissociates into a dihydrate when heated to 42°C.

### Pressure Measurements.

$$CuSO_4,(NH_4)_2SO_4,6H_2O \rightleftharpoons CuSO_4,(NH_4)_2SO_4,2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 49.9 | 26.6 | - | 26.4 |
| 30.3 | - | 5.1 | 4.8 |
| 33.8 | 6.8 | - | 6.8 |
| 40.5 | 12.9 | - | 12.8 |
| 45.9 | 19.4 | - | 19.4 |
| 51.2 | 29.3 | - | 29.2 |
| 60.5 | 55.2 | - | 56.5 |
| 77.7 | 159.6 | - | 160.3 |
| 68.8 | - | 94.3 | 95.3 |
| 60.9 | - | 57.5 | 57.9 |
| 54.5 | - | 37.2 | 36.6 |
| 48.7 | - | 24.9 | 24.2 |
| 42.8 | - | 16.2 | 15.1 |
| 35.5 | - | 8.5 | 7.9 |

### Formula.

$$\log p = 1.254 + \frac{3562}{T} - \frac{1,132,600}{T^2}$$

$$Q_{50} = 14,800 \text{ calories.}$$

The curves for the copper double sulphates are reproduced in Fig. X. Attention is drawn to the position of Caesium.

# DOUBLE SULPHATES FORMING TETRAHYDRATES ON DISSOCIATION.

## Magnesium Potassium Sulphate.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | $\%SO_4$ | 48.14 | 47.71 |
| | $\%H_2O$ | 26.70 | 26.86 |

### Dehydration.

When heated to 60°C. in an oven, the salt lost two molecules of water forming a tetrahydrate. According to van't Hoff (see Abegg's "Handbuch der Anorganischen Chemie", II, 2, 58) the hexahydrate (Schönite) loses two molecules of water at 47°C forming the tetrahydrate. (Leonite)

### Pressure Measurements.

$$MgSO_4,K_2SO_4,6H_2O \rightleftharpoons MgSO_4,K_2SO_4,4H_2O + 2H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 50.8 | 87.6 | - | 87.5 |
| 54.3 | 103.9 | - | 103.8 |
| 60.3 | 138.6 | - | 137.7 |
| 64.9 | 171.2 | - | 170.6 |
| 70.4 | 217.1 | - | 216.8 |
| 57.3 | - | 120.4 | 119.9 |
| 44.9 | - | 64.3 | 64.4 |
| 36.2 | - | 40.2 | 40.3 |
| 27.7 | - | 24.5 | 24.3 |

### Formula.

$$\log p = 6.863 - \frac{908.3}{T} - \frac{221,950}{T^2}$$

$$Q_{50} = 10,400 \text{ calories.}$$

## Magnesium Rubidium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 39.04 | 38.77 |
| $\%H_2O$ | 22.01 | 21.83 |

### Dehydration.

When heated this salt first loses water about 80°C. It was found impossible to isolate a definite hydrate, though from the manner in which the rate of loss of water slackened off after two molecules had been lost and from the relative values of the dissociation pressures of this salt and the corresponding potassium salt it may be assumed that the equilibrium pressure measured is that of hexahydrate in contact with tetrahydrate. See Fig. XI. The pressure measurements were carried out on the slightly dihydrated hexahydrate.

### Pressure Measurements.

$$MgSO_4,Rb_2SO_4,6H_2O \rightleftharpoons MgSO_4,Rb_2SO_4 4H_2O + 2H_2O \quad (?)$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 31.4 | 13.5 | - | 13.5 |
| 43.9 | 31.6 | - | 31.4 |
| 66.9 | 122.9 | - | 122.5 |
| 57.4 | 70.5 | - | 71.9 |
| 46.3 | - | 35.7 | 36.8 |
| 28.8 | - | 11.5 | 11.2 |

### Formula.

$$\log p = 7.752 - \frac{1148}{T} - \frac{264,030}{T^2}$$

$$Q_{50} = 12,700 \text{ calories.}$$

## Magnesium Caesium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 32.84 | 32.55 |
| $\%H_2O$ | 18.50 | 18.32 |

### Dehydration.

The salt loses water on heating to 75°C. The same remarks apply here as under the rubidium salt (p ).

### Pressure Measurements.

$$MgSO_4,Cs_2SO_4,6H_2O \rightleftharpoons MgSO_4Cs_2SO_4 4H_2O + 2H_2O \quad (?)$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 30.0 | 18.9 | - | 18.9 |
| 36.6 | 28.1 | - | 28.3 |
| 48.7 | 55.1 | - | 55.1 |
| 57.1 | 84.8 | - | 84.5 |
| 67.7 | 139.4 | - | 139.3 |
| 53.2 | - | 69.0 | 69.8 |

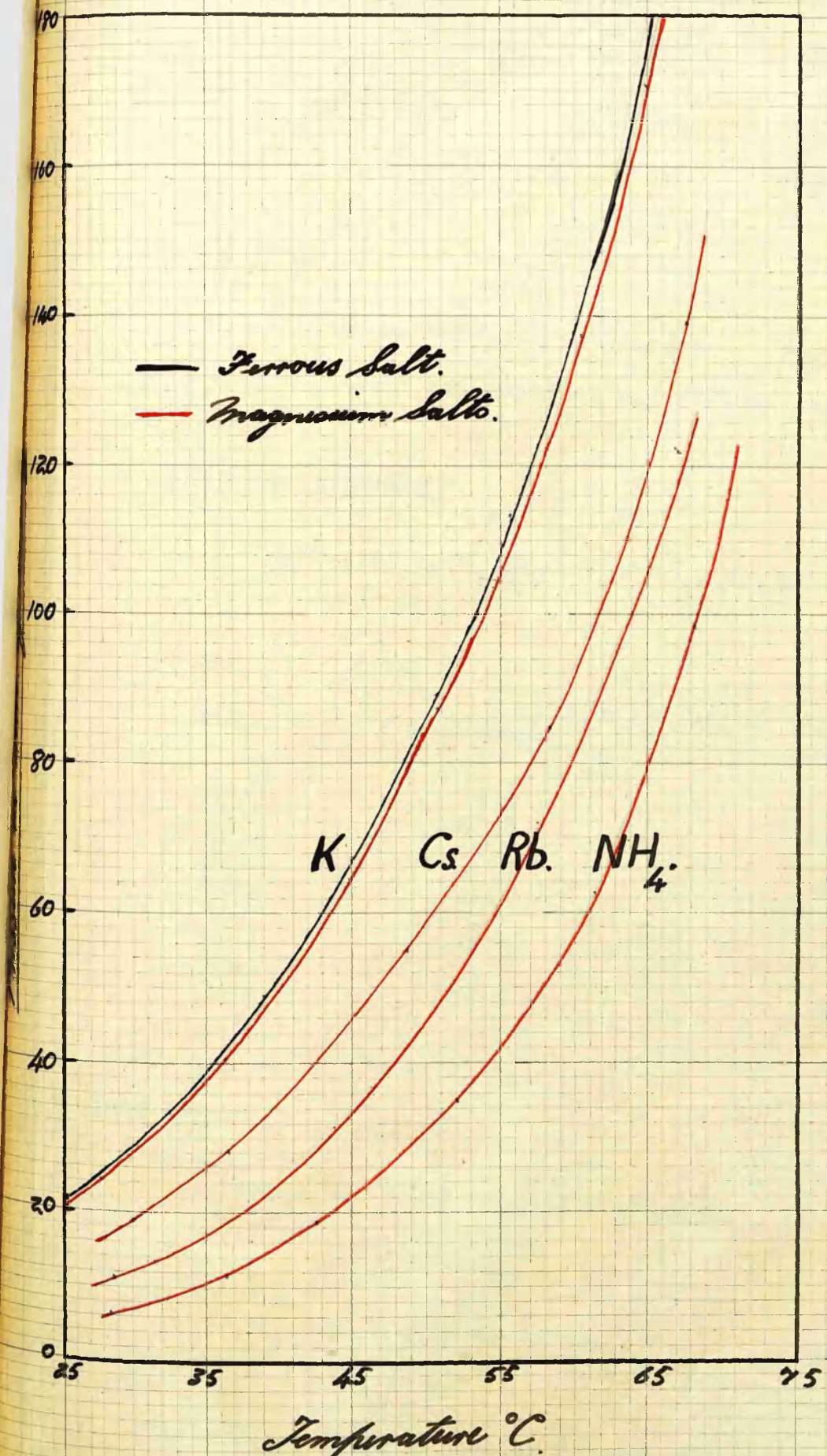
### Formula.

$$\log p = 6.597 - \frac{751.8}{T} - \frac{260,600}{T^2}$$

$$Q_{50} = 10,800 \text{ calories.}$$

# Fig XI

## Dissociation Pressure Curves of Magnesium Double Sulphate & of Ferrous Potassium Sulphate.



## Magnesium Ammonium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 53.16 | 53.28 |
| $\%H_2O$ | 29.80 | 29.97 |

Dehydration.

The salt first loses water at 75°C. The same remarks apply here as under the rubidium and caesium salts.

Pressure Measurements.

$$MgSO_4,(NH_4)_2SO_4,6H_2O \rightleftharpoons MgSO_4,(NH_4)_2SO_4 4H_2O + 2H_2O \quad (?)$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 42.8 | 18.2 | - | 18.6 |
| 48.5 | 27.3 | - | 27.6 |
| 52.1 | 35.2 | - | 34.9 |
| 61.2 | 61.2 | - | 61.5 |
| 68.2 | 92.8 | - | 92.8 |
| 43.7 | - | 19.7 | 19.9 |
| 36.3 | - | 11.5 | 11.7 |
| 28.4 | - | 6.3 | 6.2 |
| 42.9 | 18.1 | - | 18.7 |

Formula.

$$\log p = 5.383 + \frac{485.1}{T} - \frac{563,500}{T^2}$$

$$Q_{50} = 13,700 \text{ calories.}$$

The curves of the magnesium systems will be found in Fig. XI.

## Ferrous Potassium Sulphate.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%SO_4$ | 44.23 | 44.24 |
| %Fe | 12.82 | 12.86 |

### Dehydration.

The salt loses two molecules of water at 30°C. yielding a tetrahydrate. No oxidation of the salt was observed after it had been heated for four days at 50°C. in air.

### Pressure Measurements.

$$FeSO_4K_2SO_46H_2O \rightleftharpoons FeSO_4K_2SO_44H_2O + 2H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 25.1 | 21.0 | - | 21.7 |
| 32.5 | 32.9 | - | 33.7 |
| 39.0 | 48.3 | - | 48.6 |
| 45.0 | 66.9 | - | 66.8 |
| 50.7 | 89.1 | - | 88.9 |
| 55.7 | 113.3 | - | 113.5 |
| 61.7 | 148.6 | - | 148.3 |
| 49.9 | - | 85.2 | 85.7 |
| 36.2 | - | 59.4 | 59;2 |
| 26.6 | - | 23.6 | 23.8 |
| 41.2 | 54.3 | - | 54.6 |
| 66.6 | 186.8 | - | 186.6 |
| 71.5 | 228.9 | - | 229.6 |
| 51.2 | - | 91.4 | 91.2 |
| 36.6 | - | 42.0 | 42.8 |

### Formula.

$$\log p = 6.768 - \frac{866.5}{T} - \frac{224,400}{T^2}$$

$$Q_{50} = 10,400 \text{ calories.}$$

## PRESSURE MEASUREMENTS.

## II DOUBLE SELENATES.

## COPPER POTASSIUM SELENATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Cu | 11.85 | 11.86 |
| | $\%H_2O$ | 20.12 | 20.16 |

### Hydrate Formation.

The salt loses four molecules of water about 35°C. The resulting dihydrate is stable up to 100°C. It takes up water when exposed to the air, somewhat slowly, reforming the hexahydrate. In colour it is of a deeper blue than the hexahydrate.

### Pressure Measurements.

$$CuSeO_4, K_2SeO_4, 6H_2O \rightleftharpoons CuSeO_4, K_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 25.1 | 12.8 | - | 10.7 |
| 32.5 | 21.7 | - | 21.7 |
| 39.1 | 36.4 | - | 37.3 |
| 45.1 | 55.3 | - | 57.2 |
| 50.7 | 79.9 | - | 80.7 |
| 61.7 | 137.2 | - | 140.9 |
| 50.0 | - | 77.7 | 77.8 |
| 42.7 | - | 48.3 | 48.8 |
| 36.2 | - | 28.7 | 29.7 |

### Formula.

$$\text{Log } p = -14.462 + \frac{13,232}{T} - \frac{2,568,100}{T^2}$$

$$Q_{50} = 12,170 \text{ calories.}$$

## COPPER RUBIDIUM SELENATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Cu | 10.11 | 10.11 |
| | $\%H_2O$ | 17.28 | 17.19 |

### Hydrate Formation.

The salt first loses water about 60°C forming the dihydrate, which is blue in colour, and of a deeper blue than the hexahydrate.

### Pressure Measurements.

$$CuSeO_4, Rb_2SeO_4, 6H_2O \rightleftharpoons CuSeO_4, Rb_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 24.9 | 8.0 | - | 7.7 |
| 32.3 | 13.5 | - | 13.1 |
| 41.1 | 24.4 | - | 24.2 |
| 49.6 | 42.4 | - | 42.5 |
| 59.1 | 77.9 | - | 76.7 |
| 58.3 | 73.7 | - | 73.3 |
| 74.8 | 192.0 | - | 191.9 |
| 67.1 | - | 121.0 | 123.9 |
| 51.9 | - | 49.3 | 49.1 |
| 34.4 | 16.2 | - | 16.1 |

### Formula.

$$\text{Log } p = 11.044 - \frac{3162}{T} + \frac{40,160}{T^2}$$

$$Q_{50} = 13,100 \text{ calories.}$$

## COPPER CAESIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%H_2O$ | 14.80 | 14.94 |

### Hydrate Formation.

The salt forms a dihydrate when heated to 60°C.

### Pressure Measurements.

$$CuSeO_4, Cs_2SeO_4, 6H_2O \rightleftharpoons CuSeO_4, Cs_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 27.7 | 22.8 | - | 23.0 |
| 36.0 | 37.9 | - | 38.1 |
| 42.7 | 54.7 | - | 55.5 |
| 50.0 | 81.1 | - | 81.3 |
| 56.2 | 110.5 | - | 110.2 |
| 59.2 | 125.9 | - | 126.2 |
| 65.2 | 164.5 | - | 164.8 |
| 71.6 | 215.7 | | 215.8 |
| 61.2 | - | 139.1 | 138.0 |
| 51.2 | - | 86.6 | 86.1 |
| 32.3 | - | 48.7 | 49.1 |

### Formula.

$$\text{Log } p = 4.344 + \frac{707.1}{T} - \frac{482,500}{T^2}$$

$$Q_{50} = 10,400 \text{ calories.}$$

## COPPER AMMONIUM SELENATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Cu | 12.88 | 12.90 |
| | $\%H_2O$ | 21.80 | 21.88 |

### Hydrate Formation.

Four molecules of water are lost when the salt is heated just below 50°C in air, and the dihydrate formed, which is of a deeper blue than the hexahydrate.

### Pressure Measurements.

$CuSeO_4, (NH_4)_2 SeO_4, 6H_2O \rightleftharpoons CuSeO_4, (NH_4)_2 SeO_4, 2H_2O + 4H_2O.$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 25.0 | 2.8 | - | 3.0 |
| 30.6 | 5.5 | - | 5.0 |
| 35.3 | 7.5 | - | 7.5 |
| 40.0 | 10.6 | - | 11.0 |
| 45.1 | 15.3 | - | 16.5 |
| 50.8 | 26.3 | - | 25.2 |
| 54.2 | 31.8 | - | 32.0 |
| 60.3 | 48.5 | - | 48.3 |
| 64.9 | 65.0 | - | 65.2 |
| 70.4 | 90.8 | - | 91.2 |
| 57.3 | - | 38.9 | 39.7 |
| 44.9 | - | 16.2 | 16.3 |
| 36.2 | - | 8.2 | 8.1 |
| 27.7 | - | 4.1 | 3.9 |

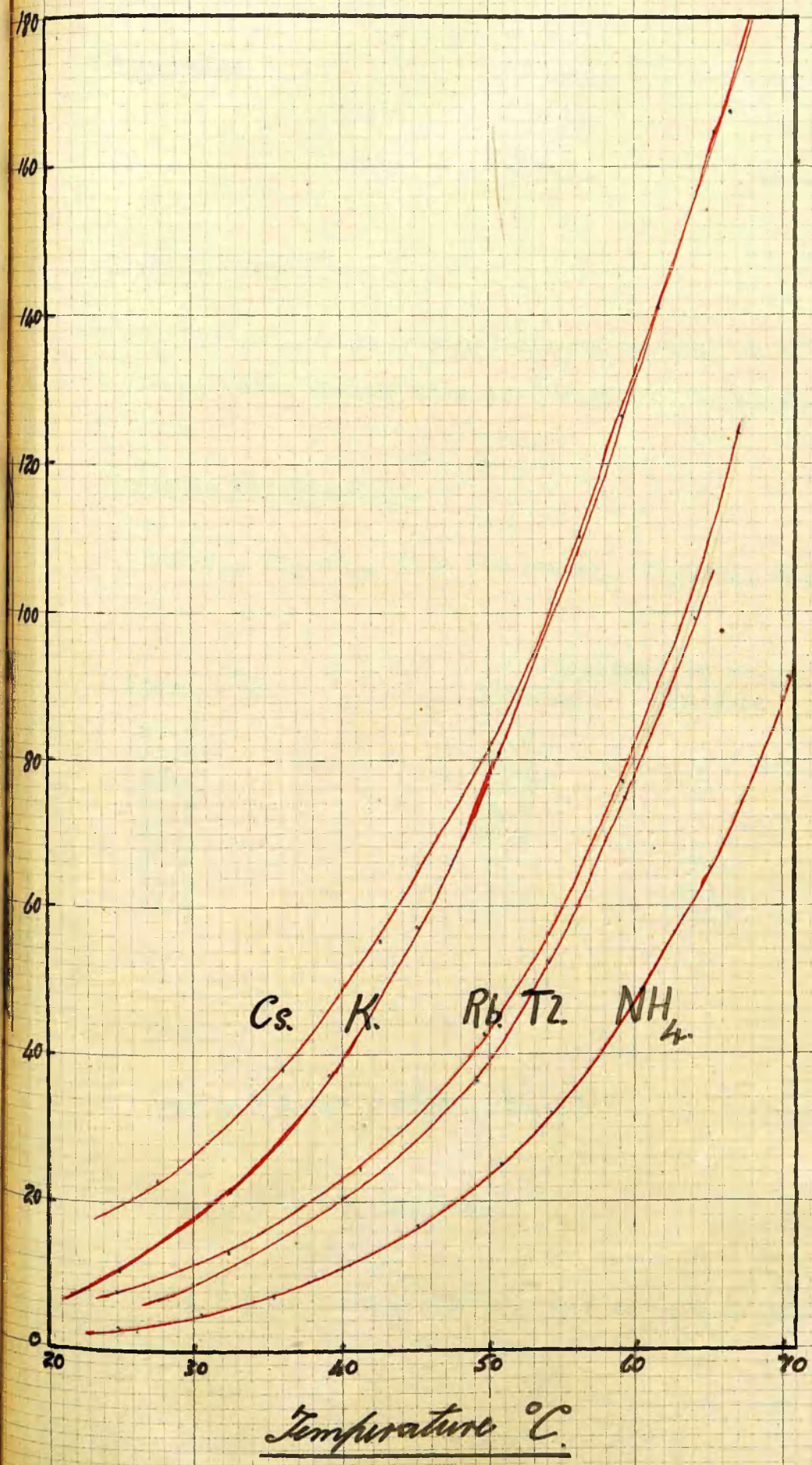
### Formula.

$$\text{Log } p = 5.456 + \frac{654.2}{T} - \frac{637,000}{T2}$$

$$Q_{50} = 15,000 \text{ calories.}$$

Fig XII

Dissociation Pressure of the Copper Double Selenate.



## COPPER THALLOUS SELENATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Cu | 7.38 | 7.34 |
| | $\%H_2O$ | 12.62 | 12.48 |

### Hydrate Formation.

The salt forms a dihydrate on heating to 70°C which is of a deeper blue colour than the original hexahydrate.

### Pressure Measurements.

$$CuSeO_4, Tl_2SeO_4, 6H_2O \rightleftharpoons CuSeO_4, Tl_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 29.9 | 8.9 | - | 9.0 |
| 40.0 | 20.3 | - | 20.2 |
| 48.0 | 36.3 | - | 36.1 |
| 53.9 | 53.6 | - | 53.3 |
| 64.1 | 99.6 | - | 99.3 |
| 59.2 | - | 75.0 | 74.5 |
| 44.5 | - | 28.7 | 28.3 |
| 35.1 | - | 13.3 | 13.8 |

### Formula.

$$\text{Log } p = 2.897 + \frac{2222}{T} - \frac{851,300}{T^2}$$

$Q_{50}$ = 13,900 calories.

The copper double selenate systems are graphed in Fig. XII.

## COBALT POTASSIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| %Co | 10.94 | 11.10 |
| $\%H_2O$ | 20.08 | 20.33 |

### Dehydration.

Like the corresponding sulphate, this salt shows the induction lag phenomenon, though not nearly so markedly. The anhydrous salt is violet, as in the case of the sulphate. The reddish-pink dihydrate is formed a little below 80°C.

### Pressure Measurements.

$$CoSeO_4, K_2SeO_4, 6H_2O \rightleftharpoons CoSeO_4, K_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 26.1 | 21.4 | - | 21.9 |
| 33.0 | 33.5 | - | 33.7 |
| 38.3 | 46.8 | - | 46.1 |
| 42.5 | 58.5 | - | 58.3 |
| 48.5 | 79.9 | - | 80.0 |
| 52.4 | 97.5 | - | 97.3 |
| 61.2 | 148.5 | - | 147.2 |
| 68.2 | 199.2 | - | 199.1 |
| 43.8 | - | 62.4 | 62.7 |
| 28.4 | - | 26.8 | 25.5 |
| 42.9 | 60.8 | - | 60.1 |

### Formula.

$$\text{Log } p = 4.245 + \frac{791.2}{T} - \frac{496,530}{T^2}$$

$$Q_{50} = 10,400 \text{ calories.}$$

## COBALT AMMONIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| %Co | 12.14 | 12.05 |
| $\%H_2O$ | 22.24 | 22.09 |

### Dehydration.

The salt behaves like the potassium salt, only requiring a higher temperature (90°C.) for the formation of the dihydrate.

### Pressure Measurements.

$$CoSeO_4, (NH_4)_2SeO_4, 6H_2O \rightleftharpoons CoSeO_4, (NH_4)_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 27.0 | 3.4 | - | 3.3 |
| 34.1 | 5.9 | - | 5.9 |
| 41.5 | 10.3 | - | 10.5 |
| 56.3 | 29.7 | - | 29.7 |
| 65.6 | 53.1 | - | 54.1 |
| 68.4 | 64.8 | - | 64.3 |
| 71.1 | 75.5 | - | 75.5 |

### Formula.

$$\text{Log } p = 8.416 - \frac{1439}{T} - \frac{279,200}{T2}$$

$$Q_{50} = 14,500 \text{ calories.}$$

## ZINC POTASSIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%H_2O$ | 19.96 | 20.04 |

### Dehydration.

Zinc potassium selenate, unlike the corresponding sulphate does not show any induction phenomenon. When heated over 70°C in air it passes directly into the dihydrate.

### Pressure Measurements.

$$ZnSeO_4, K_2SeO_4, 6H_2O \rightleftharpoons ZnSeO_4, K_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 31.3 | 23.6 | - | 23.8 |
| 42.6 | 50.7 | - | 51.6 |
| 48.5 | 75.4 | - | 74.0 |
| 57.2 | 120.3 | - | 118.0 |
| 71.3 | 218.3 | - | 216.3 |
| 59.9 | - | 136.2 | 137.8 |
| 37.2 | - | 36.2 | 35.8 |

### Formula.

$$\text{Log } p = -5.898 + \frac{7586}{T} - \frac{1,636,000}{T^2}$$

$$Q_{50} = 11,600 \text{ calories.}$$

## ZINC AMMONIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| $\%H_2O$ | 17.00 | 17.14 |

### Hydrate Formation.

This salt, like the corresponding sulphate, and unlike zinc potassium selenate, shows the induction phenomenon. The dihydrate is finally obtained by heating the salt between 70°C and 80°C

### Pressure Measurements.

$ZnSeO_4,(NH_4)_2\ SeO_4,\ 6H_2O \rightleftharpoons ZnSeO_4,(NH_4)_2\ SeO_4,\ 2H_2O + 4H_2O.$

| Temp. °C. | Pressure in mm. of mercury. Rising | Falling | Calculated. |
|---|---|---|---|
| 31.3 | 2.9 | - | 2.8 |
| 42.6 | 6.9 | - | 6.7 |
| 48.5 | 10.1 | - | 10.4 |
| 57.2 | 19.9 | - | 18.8 |
| 71.3 | 46.5 | - | 47.1 |
| 59.9 | - | 22.8 | 22.6 |
| 37.2 | - | 4.1 | 4.5 |

### Formula.

$$\log p = 10.173 - \frac{2674}{T} - \frac{86,990}{T^2}$$

$Q_{50}$ = 15,000 calories.

## NICKEL POTASSIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| %Ni | 10.85 | 11.04 |
| $\%H_2O$ | 20.02 | 20.34 |

### Dehydration.

The salt behaves similarly to the corresponding sulphate, forming the dihydrate when heated to a little below 80°C.

### Pressure Measurements.

$$NiSeO_4, K_2SeO_4, 6H_2O \rightleftharpoons NiSeO_4, K_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 29.9 | 11.9 | - | 12.3 |
| 40.0 | 25.3 | - | 25.6 |
| 48.0 | 44.4 | - | 44.3 |
| 53.9 | 63.9 | - | 64.6 |
| 64.1 | 119.0 | - | 119.1 |
| 59.2 | - | 88.7 | 89.1 |
| 44.5 | - | 35.8 | 35.1 |
| 35.1 | - | 18.3 | 18.1 |

### Formula.

$$\text{Log } p = 7.740 - \frac{969}{T} - \frac{316,900}{T2}$$

$$Q_{50} = 13,400 \text{ calories.}$$

## NICKEL RUBIDIUM SELENATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Ni | 9.32 | 9.40 |
| | $\%H_2O$ | 17.11 | 17.32 |

### Hydrate Formation.

Forms a dihydrate when heated to 105°C., after exhibiting the usual induction period.

### Pressure Measurements.

$NiSeO_4, Rb_2SeO_4, 6H_2O \rightleftharpoons NiSeO_4, Rb_2SeO_4, 2H_2O + 4H_2O$

| Temp. °C. | Pressure in mm. of mercury. Rising | Falling | Calculated. |
|---|---|---|---|
| 30.2 | 1.5 | - | 1.7 |
| 38.2 | 3.1 | - | 3.1 |
| 52.3 | 9.0 | - | 8.6 |
| 62.0 | 16.0 | - | 16.3 |
| 75.9 | 37.9 | - | 38.7 |
| 54.2 | - | 9.9 | 9.7 |
| 45.0 | - | 5.3 | 5.1 |

### Formula.

$$\log p = 10.177 - \frac{2845}{T} - \frac{52,810}{T^2}$$

$$Q_{50} = 14,500 \text{ calories.}$$

# NICKEL CAESIUM SELENATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Ni | 8.17 | 8.29 |
| | $\%H_2O$ | 15.04 | 15.32 |

## Hydrate Formation.

The salt shows the usual induction period when heated. Finally forms a dihydrate when heated to 100°C.

## Pressure Measurements.

$$NiSeO_4, Cs_2SeO_4, 6H_2O \rightleftharpoons NiSeO_4, Cs_2SeO_4, 2H_2O + 4H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 30.2 | 15.8 | - | 16.2 |
| 38.2 | 26.8 | - | 27.1 |
| 52.3 | 59.4 | - | 59.0 |
| 62.0 | 95.9 | - | 92.7 |
| 75.9 | 157.4 | - | 160.7 |
| 54.2 | - | 64.8 | 65.0 |
| 45.0 | - | 39.8 | 40.4 |

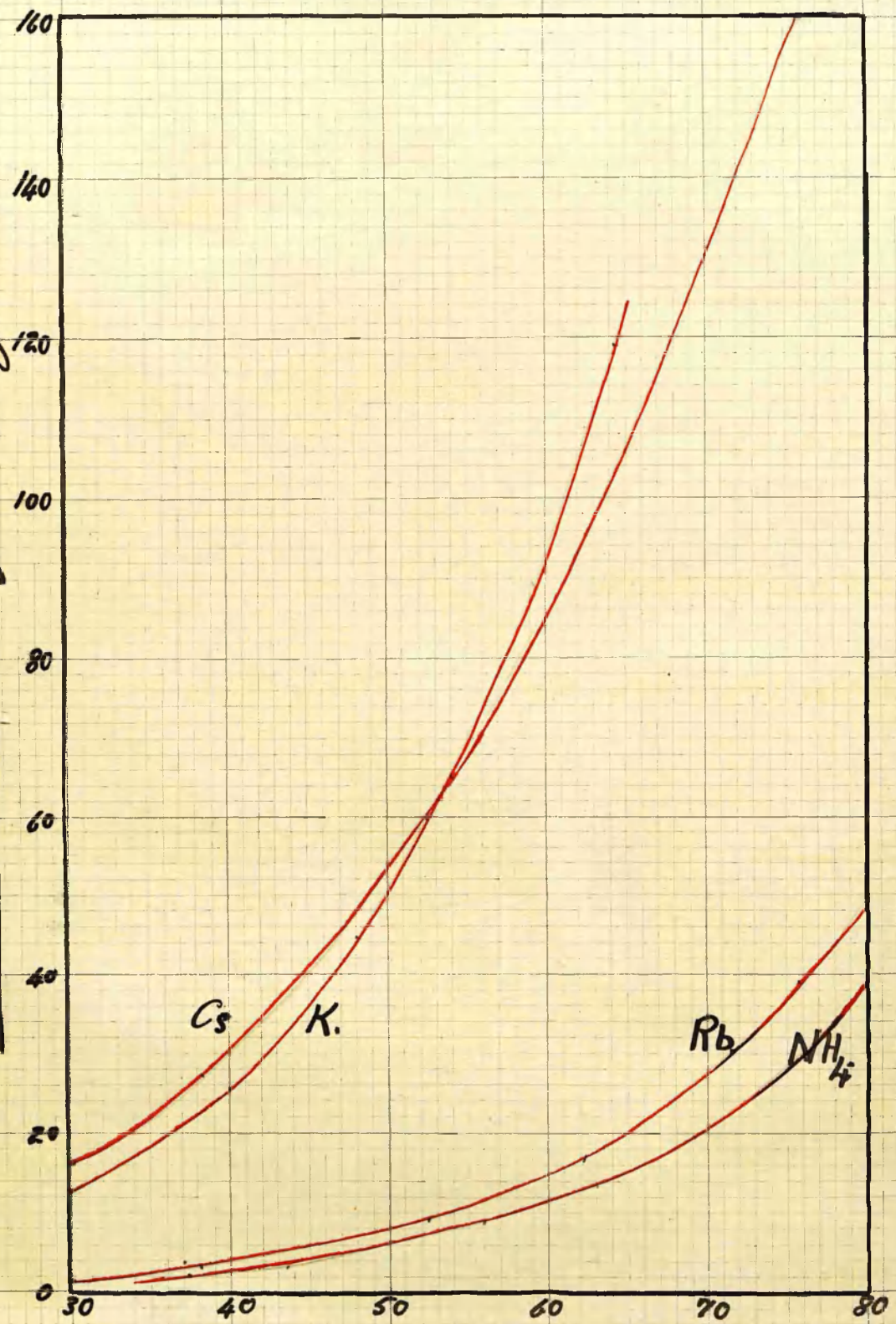
## Formula.

$$\text{Log } p = -0.322 + \frac{3651}{T} - \frac{966,170}{T2}$$

$$Q_{50} = 10,600 \text{ calories.}$$

Fig XIV

The Dissociation Pressure Curves of the Nickel Double Selenates.



## NICKEL AMMONIUM SELENATE.

| Analysis. | Found. | Calc. |
|---|---|---|
| %Ni | 11.87 | 11.99 |
| $\%H_2O$ | 21.94 | 22.10 |

### Hydrate Formation.

Forms a greenish yellow dihydrate when heated carefully to 90°C in air.

### Pressure Measurements.

$$NiSeO_4, (NH_4)_2 SeO_4, 6H_2O \rightleftharpoons NiSeO_4 (NH_4)_2 SeO_4 2H_2O + 4H_2O$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculated. |
|---|---|---|---|
| 28.3 | 1.0 | - | 0.9 |
| 37.2 | 2.0 | - | 2.0 |
| 43.6 | 3.2 | - | 3.3 |
| 56.0 | 8.2 | - | 8.3 |
| 63.2 | 13.9 | - | 13.6 |
| 69.0 | 20.3 | - | 19.8 |
| 77.0 | 32.2 | - | 32.4 |
| 57.5 | - | 9.2 | 9.2 |
| 45.2 | - | 3.9 | 3.7 |
| 35.6 | - | 1.7 | 1.7 |

### Formula.

$$\text{Log } p = 6.497 - \frac{346.1}{T} - \frac{489,800}{T^2}$$

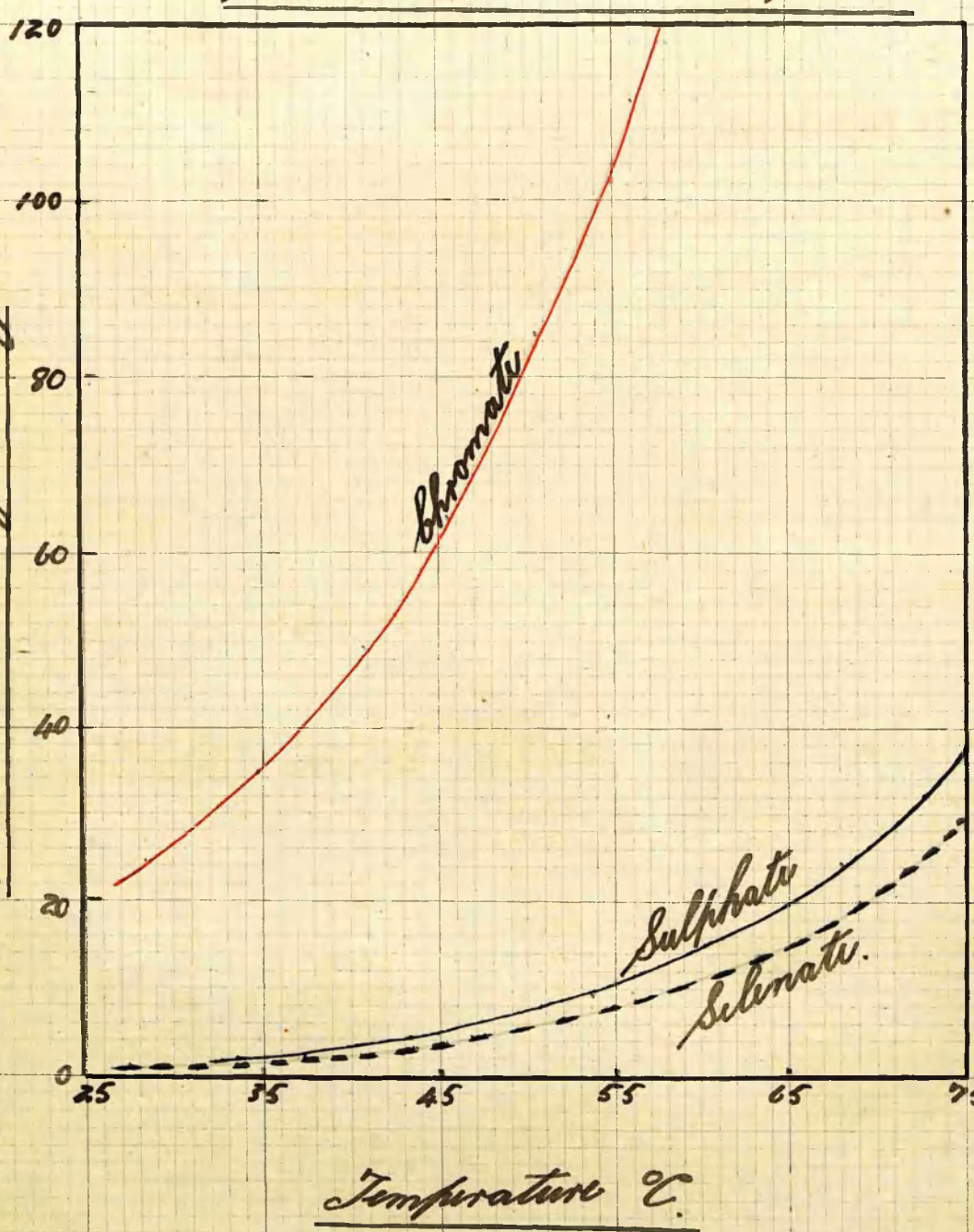
$Q_{50}$ = 15,400 calories.

The curves of the nickel double selenates are shown in Fig. XIV.

# Fig XV

## Dissociation Pressure Curves of:

Nickel Ammonium Sbromate.
Nickel Ammonium Selenate
Nickel Ammonium Sulphate.



## NICKEL AMMONIUM CHROMATE.

| Analysis. | | Found. | Calc. |
|---|---|---|---|
| | %Ni | 13.53 | 13.50 |
| | $\%H_2O$ | 24.80 | 24.86 |

### Hydrate Formation.

The salt effloresces slowly in air forming a brown substance which has the composition of the anhydrous salt. The dissociation pressures of a mixture of these two substances were measured.

### Pressure Measurements.

$$NiCrO_4,\ (NH_4)_2CrO_4,\ 6H_2O \rightleftharpoons NiCrO_4,\ (NH_4)_2CrO_4 + 6H_2O.$$

| Temp. °C. | Pressure in mm. of mercury. Rising. | Falling. | Calculator. |
|---|---|---|---|
| 28.2 | 23.8 | - | 24.3 |
| 34.8 | 34.8 | - | 34.4 |
| 40.8 | 49.4 | - | 49.4 |
| 45.3 | 64.4 | - | 63.8 |
| 50.7 | 84.7 | - | 84.9 |
| 43.2 | - | 56.3 | 56.9 |
| 37.0 | - | 40.0 | 39.5 |
| 43.7 | 58.6 | - | 58.5 |
| 56.0 | 111.7 | - | 111.2 |
| 63.2 | 155.6 | - | 155.6 |
| 69.0 | 201.7 | - | 200.4 |
| 76.7 | 278.0 | - | 275.4 |
| 57.4 | - | 117.8 | 119.1 |
| 35.6 | - | 36.7 | 36.4 |
| 27.7 | | 22.8 | 21.6 |

### Formula.

$$\text{Log } p = 2.903 + \frac{1729}{T} - \frac{661,620}{T2}$$

$$Q_{50} = 15,400 \text{ calories.}$$

## DISCUSSION OF RESULTS.

It is assumed in the following discussion that the magnitude of the aqueous vapour pressure over a hydrated salt in equilibrium with the next lower hydrate is a measure of the strength of the forces holding the water of crystallisation in the molecule.

It is unlikely that a priori considerations will give much help in indicating the strength of these forces. The constitution of compounds containing water of crystallisation is practically unknown, unless we accept a few vague suggestions of Werner or of Rhodes (Chem. News, 1921, pp. 85, 97). X-ray analysis should give some help here, but so far, apparently, only the water of crystallisation of the alums has been thus investigated (Vegard and Schelderup,[17] Ann. Physik., 1917, 54, 146; Wyckoff,[18] Amer. J. Sci. 1923, 5, 15). These two investigations differ as to the structure to be assigned to the space lattice; and beyond the fact that the water of crystallisation forms a structural component of the grating system, and that no distinction can be drawn between water of crystallisation and water of constitution, little light is thrown on the present problem.

Apart from the water of crystallisation, the structures of the anhydrous double salts studied in the present investigation are probably of the types $M_2\ R(SO_4)_2$ and $M_2\ R(SeO_4)_2$, where M and R have their usual signification. Support is given to this formula by the fact of the existence of complex ions containing the bivalent metal, in aqueous solutions of the salts. Thus Pfanhauser[19] has shown, (Zeit. Elektrochem., 1901, 7, 698), that in saturated solutions of nickel ammonium sulphate at ordinary temperatures, the ions are mostly $NH_4^{\bullet}$ and $Ni(SO_4)_2^{1}$. Reiger[20] (Zeit. Elektrochem., 1901, 7, 863) has also shown that

in solutions of copper potassium sulphate, the copper migrates partially to the anode.

Hence in what follows, the alkali metals of the double salts will be designated as the cationic metals and the bivalent metals as the anionic metals.

Returning to the dissociation pressures, it might be expected that the crystallographic character of the salt would have a large influence in determining the value of the dissociation pressure. This influence is, however, not noticeable in the present case. Thus Tutton,[1] (J.C.S., 1893, 63, 337), has pointed out that replacement of the bivalent metal in the isomorphous series of the double sulphates by another brings about only slight changes in the crystallographic constants, but that replacement of the alkali metal brings about relatively large changes. In the case of the dissociation pressures alteration of the bivalent or univalent metals, may bring about changes of the same order of magnitude. Again the crystallographic properties of these salts alter in a definite progression with increase of the atomic number of the alkali metal. The values of the dissociation pressures, at constant temperature of salts with the same bivalent metal, decrease, in most cases in the order K, Cs, Rb, whereas the atomic numbers, of course, increase in the order K, Rb, Cs.

Ephraim,[2] (Berichte, 1912, 45, 1322) has pointed out the influence of atomic and molecular volume in determining the stability of ammine molecules, and has also treated the stability of hydrates from this point of view.

In Table IV are given the molecular volumes of the salts examined, and also the absolute temperatures at which the dissociation pressures attain a definite value (50 mm.). This temperature is assumed to be a measure of the stability of the hydrate. The molecular volumes are taken from the latest results of Tutton.

TABLE IV.

| Alkali Metal. | Bivalent Metal. | Sulphates. $T_{50}$ | Sulphates. M.V. | Selenates. $T_{50}$ | Selenates. M.V. |
|---|---|---|---|---|---|
| Potassium | Copper | 320.8 | 197.8 | 316.6 | 211.3 |
| | Cobalt | 325.9 | 197.1 | 312.5 | 208.6 |
| | Zinc | 327.8 | 196.2 | 315.2 | 208.8 |
| | Nickel | 336.5 | 195.3 | 323.9 | 206.1 |
| Rubidium | Cadmium | 313.5 | 216.4 | - | - |
| | Manganese | 315.2 | 213.7 | - | - |
| | Copper | 326.0 | 207.7 | 325.0 | 221.5 |
| | Cobalt | 335.0 | 206.5 | - | - |
| | Zinc | 339.0 | 205.6 | - | - |
| | Nickel | 346.3 | 204.8 | 354.0 | 217.0 |
| Caesium | Cadmium | 315.0 | 229.3 | - | - |
| | Manganese | 319.9 | 226.4 | - | - |
| | Copper | 332.5 | 220.3 | 314.1 | 235.5 |
| | Cobalt | 334.0 | 219.7 | - | - |
| | Zinc | 336.8 | 218.0 | - | - |
| | Nickel | 345.0 | 217.4 | 322.8 | 229.2 |
| Ammonium | Cadmium | 317.3 | 217.5 | - | - |
| | Manganese | 317.2 | 215.5 | - | - |
| | Copper | 332.0 | 207.7 | 333.7 | 222.2 |
| | Cobalt | 336.8 | 208.0 | 337.2 | 218.1 |
| | Zinc | 341.4 | 206.4 | 345.0 | 217.7 |
| | Nickel | 354.0 | 205.5 | 358.0 | 216.5 |
| Potassium | Ferrous | 312.2 | 198.1 | - | - |
| | Magnesium | 313.3 | 196.6 | - | - |

On examining this table it will be seen that in the case of double salts formed by the same alkali metal with different bivalent metals, the temperature at which a pressure of 50 mm. is attained increases with decreasing molecular volume, i.e. the smaller the molecular volume of double salts containing the same alkali metal, the more firmly is the water held in the molecule. The molecular volumes of such groups of salts are of course dependent on the atomic volumes of the bivalent metals. If we take the atomic radii of the bivalent metals according to Bragg[22] (Phil. Mag. 1920, 40, 169) we have the following diminishing order;

| Metal | Atomic Radius X $10^8$ |
|---|---|
| Cd | 3.2 Kmu. |
| Mn | 2.95 |
| Cu | 2.75 |
| Co | 2.75 |
| Ni | 2.70 |
| Zn | 2.65 |

On consulting Table IV it will be seen that this is roughly the order of increasing $T_{50}$ for each group of alkali double sulphates or selenates containing these metals.

This leads to the conclusion that stability is favoured by diminishing molecular volume of the anion or negative part of the molecule. As the selenates have in all cases much greater molecular volumes than the sulphates they would be expected to be less stable. This is the case with the double selenates of caesium and potassium, but not with those of ammonium and rubidium, which are more stable than the corresponding sulphates. The double chromate examined (p. 64 ) was the least stable of the three nickel ammonium salts, the chromate, the sulphate and the selenate. Its molecular volume

is also the highest, but in this case it must be remembered that we are not dealing with comparable types of equilibrium, the sulphate and selenate forming dihydrates, whilst the chromate yields only the anhydrous salt on loss of water.

As regards the influence of the alkali metal, this is found to be rather complex. In the sulphate groups. $T_{50}$ increases in the order K, Cs, Rb, $NH_4$ in most cases (Co, Zn, Ni, Mg), whereas with copper, manganese and cadmium the order of increasing $T_{50}$ is K, Rb, $NH_4$, Cs. The former group of metals are alike in that their simple sulphates are heptahydrated, whereas, the sulphates of the latter group do not form stable heptahydrates. In the selenates, in the two cases examined (copper and nickel), the order is Cs, K, Rb, $NH_4$.

The Molecular volumes of the salts with the same bivalent metal always increase in the order K, Rb., $NH_4$, Cs, whilst the atomic radii of the alkali metals according to Bragg (loc. cit.) are

| | |
|---|---|
| K | 4.15 |
| Rb | 4.50 |
| Cs | 4.75 |

In the following table are given the dissociation pressure of systems of the type $RSO_4\ 7H_2O$ - $RSO_4\ 6H_2O$ - water vapour where R is Mg, Fe, Zn, Co, or Ni, determined by Schumb[23] (J. A.C.S. 1923, 45, 342); and also the atomic radii of the metals R

| Salt | Pressure at 25°C | Atomic Radius $\times 10^{8}$ |
|---|---|---|
| $MgSO_4$ | 12.50 | 2.85 cm. |
| $FeSO_4$ | 14.56 | 2.80 |
| $ZnSo_4$ | 15.34 | 2.65 |
| $CoSO_4$ | 16.58 | 2.75 |
| $NiSO_4$ | 20.69 | 2.70 |

Except in the case of zinc, which is out of place, the order of increasing dissociation pressure is that of diminishing atomic radius, i.e., the order of increasing $T_{50}$ would be one of increasing atomic radius.

It is interesting to compare this table with that on p 67. The conditions are reversed. In this case the bivalent metal forms the positive part of the molecule, whereas in the double salts it forms part of the negative portion of the molecule. In the latter case we find that diminishing atomic radius brings about increased stability, and in the former decreased stability. In each case it is interesting to note that zinc is out of place.

It may be suggested that increasing molecular volume of the alkali metal in the double salt series confers increasing stability on the molecule, but that there is an opposing tendency in the increasing volume of the molecule as a whole. This will account for the order K, Cs, Rb, $NH_4$, as the caesium salts have by far the largest volume. In the case of cadmium and manganese the molecule is already large owing to the pressure of the bivalent metal, so that the stabilising action of the large volume of the cationic metal comes into play, and we get the caesium salts more stable than the rubidium salts. Copper thus still remains an exception. Tutton (loc. cit.) has shown that the copper double sulphates are markedly differentiated from the others in their crystallographic characters.

Biron (J. Russ. Phys. Chem. Soc., 1915, 47, 964; Chem. Soc. Abs. 1915, ii, 762) has pointed out that in the sub-groups of the Periodic System the properties of compounds of the elements may vary, not progressively, but periodically as the atomic weight increases. With the groups P, As, Sb, Cl, Br, I; S, Se, Te, the affinity towards oxygen does not vary continuously in any one period, but is least for the

middle element in each case. Biron considers that an explanation is to be found in Abegg's theory of two-fold valencies. It is found that the elements of the sub-groups form triads, the compounds of which exhibit physical and chemical properties (1) varying regularly when the compounds are formed with normal valencies and (2) showing secondary periodicity when the compounds are formed with contra-valencies.

This may have some bearing on the order of stability of the hydrates of the alkali double sulphates which in most cases is K, Cs, Rb.

The influence of molecular volume is well exemplified in the cases of ammonium and thallium. Tutton has shown that the molecular volumes of ammonium and thallium double selenates lie close to those of the rubidium salts. If the dissociation pressure curves are examined (Figs V-XV) it will be seen that the ammonium salt curves lie close to and always below the rubidium salt curves. The dissoci-:ation pressures of the two thallium salts investigated (copper thallous selenate and sulphate) also lie close to and below the rubidium salt curves. The atomic radii of thallium and rubidium are both equal to 4.5 according to Bragg.

It is by no means suggested that molecular volume is the sole determining factor in the stability of these compounds. Specific action of the various metals and groups obviously enters. The high values of $T_{50}$ in the case of nickel salts, especially nickel ammonium selenate, seem out of proportion to the value of their molecular volumes, and, as we have just seen, copper presents anomalies. Again, the fact that in a few cases the curves intersect, renders generalisation precarious.

Clark & Buckner[26] (J.A.C.S., 1922, 44, 242)[2] and Clark[25] (Amer. Journ. Sci., 1924, 7, 1) have carried out a long series of measurements of the stabilities of ammines of inorganic salts, as indicated by the temper-:ature at which the vapour pressures of the ammine rises to a definite value (100 or 760 mm.). They have found that the stability increases with diminishing atomic volume of the positive part of the molecule, e.g., in the series Cs, Rb, K, Na; Cd, Zn, Mn, Cu, Fe.), and increases with increasing volume of the negative part, e.g., in the series Cl, Br, I; $MoO_4$, $CrO_4$, $SO_4$, $SeO_4$.

In the case of hydrates, as we have seen, the condition of affairs is exactly opposite. Stability in this case diminishes with increasing volume of the negative part of the molecule, and seems to vary period-:ically with the volume of the positive portion, increasing at first as the atomic volume increases.

Clark & Buckner (loc. cit.) find that the stabilities of ammines are directly proportional to increasing difference in volume between anion and cation. This is not the case with the stabilities of the hydrates exam-:ined in the present investigation, as the potassium salts in which this difference is greatest are in nearly every case the least stable.

Thus water behaves in the opposite manner to ammonia. Clark states that ammonia is attracted solely by the cation, whereas water may also be attracted by the anion. This fact probably accounts for the rather complex relationships brought to light in the present investi-:gation where caesium forms the positive part of the molecule, the order of increasing stability being generally K, Cs, Rb, $NH_4$.

## SUMMARY.

1. The hydrates formed by double sulphates and selenates of the types: $RSO_4$, $M_2SO_4$, $6H_2O$ and $RSeO_4$, $M_2SeO_4$, $6H_2O$ have been investigated. As far as has been investigated, the iron and magnesium salts first form tetrahydrates on loss of water, all the other salts forming dihydrates.

2. An induction lag in the dehydration of the hexa-:hydrated salts has been studied.

3. The dissociation pressures of the hexahydrated salts in equilibrium with their next lower hydrates have been measured over a range of temperatures.

4. The stabilities of the hydrates, as indicated by the absolute temperatures at which the pressure attains a value of 50 mm., show a close relation with the mole-:cular volumes of the salts, and with the atomic volumes of their constituents.

5. The stabilities of the hydrates increase with diminishing volume of the negative portion of the molecule, considering the sulphate and selenate groups separately.

6. The stabilities of the hydrates show a tendency to increase with increasing volume of the positive portion of the molecule except in the case of caesium, the general order being K, Cs, Rb, $NH_4$, in the case of the sulphates, and Cs, K, Rb, $NH_4$ in the case of the selenates. When the bivalent metal is either copper, cadmium, or manganese, the order is K, Rb, $NH_4$, Cs, in the case of the sulphates.

7. These relations are the opposite of what obtains with that other large class of auxiliary valency compounds, - the inorganic ammines.

8. The ammonia and thallium salts furnish dissociation pressures which, in magnitude, approach more nearly to those of the rubidium salts than those of the potassium and caesium salts. This relationship to rubidium is in accord with the results of Tutton (loc. cit.), and is considered due to the similarity in molecular volume of the rubidium, ammonium, and thallium salts.

# BIBLIOGRAPHY.

## Bibliography.


1. "Chemical and Physical Researches", by Thomas Graham, printed for presentation at Edinburgh, 1876.

2. "Connection between the Atomic Weight of contained Metals and the magnitude of the Angles of Crystals of Isomorphous Series," by Alfred E. Tutton, - Journal of the Chemical Society, 1893, 63, 337.

3. "Monoclinic Double Selenates of the Manganese and Cadmium Groups," by Alfred E. Tutton. - Proceedings of the Royal Society, 1922, (A), 101, 225.

4. "Text Book of Inorganic Chemistry" edited by J. N. Friend. Vol. II, p.229.

5. "Über die Natur der Nebenvalenzen. XVI : Haftintensität des Wassers in Krystallwasser - Verbindungen," von Fritz Ephraim und Paul Wagner - Berichte, 1917, 50, 1089.

6. "A Period of Induction in the Dehydration of Some Crystalline Hydrates," by William Norman Rae. - Journal of the Chemical Society 1916, 109, 1229.

7. "The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method," by James R. Partington. - Journal of the Chemical Society, 1911, 99, 475.

8. "Selenic Acid and Copper Selenate," by L. M. Dennis and J. P. Koller. - Journal of the American Chemical Society, 1919, 41, 949.

9. "Sur le séléniate de cuivre et son emploi à la préparation de l'acide sélénique," par M. R. Metzner, - Comptes Rendus, 1898, 127, 54.

10. "A Series of Double Chromates," by Samuel H. C. Briggs, - Journal of the Chemical Society, 1903, 83, 392.

11. "The Isolation of Stable Salt Hydrates, with Special Reference to the Stable Hydrates of Sodium Carbonate," by Alexander Charles Cumming. - Journal of the Chemical Society, 1910, 97, 596.

12. "Examination of Substances by the Time Method," by J. B. Hannay. - Journal of the Chemical Society, 1877, 32, 381.

13. "On the Dehydration of Hydrates by the Time Method. Part I, Iron and Aluminium Hydrates," - by William Ramsay. - Journal of the Chemical Society, 1877, 32, 395.

14. "The Dissociation Pressures of the Alkali Bicarbonates," by R. M. Caven and H. J. S. Sand. - Journal of the Chemical Society, 1911, 99, 1359; 1914, 105, 2752.

15. "Über die Dissociationsdrucke einiger Metallhydroxyde und Carbonate," von J. Johnston. - Zeitschrift für physikalische Chemie, 1908, 62, 330.

16. "Handbuch der Anorganischen Chemie." - Gmelin - Kraut - Vol. IV. p. 157.

17. "Die Kristallstrucktur der Alaune und die Rolle des Kristallwassers," von L. Vegard und H. Schjelderup. - Annalen der Physik, 1917, 54, 146.

18. "The Crystal Structure of the Alums," by Ralph W. G. Wyckoff. - Americal Journal of Science, 1923, 5, 15.

19. "Über das Elektrochemische Verhalten des Nickellammon-:sulfates," von W. Pfanhauser. - Zeitschrift für Elektrochemie, 1901, 7, 698.

20. "Über die Konstitution Halbkomplexer Salze nach ihrer Elektrolytischen Überführung," von E. Rieger. - Zeitschrift für Elektrochemie, 1901, 7, 863.

21. "Über die Natur der Nebenvalenzen Erste Mitteilung : Metallammoniak Verbindungen," von Fritz Ephraim, - Berichte, 1912, 45, 1322.

22. "The Arrangement of Atoms in Crystals," by W. L. Bragg.- Philosophical Magazine, 1920, 40, 169.

23. "The Dissociation Pressures of Certain Salt Hydrates by the Gas Current Saturation Method," by Walter C. Schumb. - Journal of the American Chemical Society, 1923, 45, 342.

24. "The Existence of Ammonium Hydroxide as a Base," by R. M. Caven. - Chemistry and Industry, 1923, 164, 448, 744.

25. "Secondary Valence in the Light of Recent Researches I. Inorganic Ammines," by G. L. Clark. - American Journal of Science, 1924, 7, 1.

26. "The Properties of Subsidiary Valence Groups," by George L. Clark and Henry K. Buckner.

27. "The Application of Friend's Theory of Valency to Water of Crystallisation," by Rhodes. - Chemical News, 1921, 85, 97.